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Analysis and Treatment of a male portrait in oil and a study of the size layer with reconstructions from Vibert's recipe (1892)

Dissertação para obtenção do Grau de Mestre em Conservação e Restauro

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Novembro 2015

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ACKNOWLEDGMENTS

''It always seems impossible until it's done.'' – Nelson Mandela

Throughout this year, there was a feeling that such project was impossible to be complete, but thanks to people that I met, who taught me and made me grow both professionally and personally, I can finally say: it's done. I have to thank in particular:

Primarily, I would like to give the biggest and most sincere thanks to a person that I admire a lot: my supervisor Leslie Carlyle, for her work, knowledge, and enthusiasm. Her attention and support were crucial, since that was what kept me going to do bigger and better. Her pleasant words were constantly motivating me. It has been a great honour to work by your side and to be one of your Master's students.

To my co-supervisor Isabel Pombo Cardoso, for always being very logical and providing lucid comments throughout this year. Her generous guidance during analysis was very important and I am very grateful. Besides the work of this project, I had entertaining moments which always cheered me up.

Raquel Marques, my ''twin sister'', who always read my thoughts and made the hours spent in the laboratory much more hilarious. I enjoyed every moment we had to share ideas as well as creating good relationships. I hope to continue having your friendship.

To my colleagues Sara and Leonor, we always supported each other's work and during moments of frustration, one of us always had the capability of making the others laugh. I hope you enjoyed this year as much as I did.

This project could not have been done without the opportunity conceived by Colecção Caixa Geral de Depósitos. Special thanks to Isabel Corte-Real and Inês Dias for the information provided and for allowing me to know better the collection displayed in storage.

To José Rodrigues, Ana Alves and Sara Santos from Instituto Superior de Agronomia, for their generosity, interest and help during pyrolysis analysis.

To the doctoral students, in specific Marta, Vanessa, Tatiana, Élia, Diogo, Joana, Susana and Sara Babo for the wise advices and for the laughs when most needed.

To the professors from the DCR: Professor Maria João Melo, for the availability to accomplish µ-FTIR analysis, as well as the precise advices given and for the passion and accurateness of teaching us students; Professor Márcia Vilarigues for the support and interesting discussions.

To Ana Maria who helped me during these five years when I needed. Her smile and nice words always have the capacity of enriching the day of anybody.

To my best friends Ana Sabala and Nadine, for all the support, moments, friendship and laughs we take with us from these years in Faculty. And of course to my friends Escada, Artur, André, Horta, Mariana, Marta, Sara and Mafalda. The best five years of my life were spent with all of you, by constantly sharing true friendship and remarkable moments. I wish the best of the successes to each and every one of you throughout the upcoming years.

To my family, especially my parents and brother, that were constantly supporting and encouraging me (especially when I was frustrated). Your unconditional love and strength was very important this year and I hope I made you proud.

Lastly, I particularly dedicate every effort of this dissertation to my grandparents Carlos and Elizabeth, who always believed in my capabilities and cheered me. You both mean a lot to me.

RESUMO

Este projecto de tese focou-se no estudo e tratamento de um retrato masculino a óleo, do início do século XX, pertencente à Colecção Caixa Geral de Depósitos, Lisboa, Portugal. O retrato de *Januário Correia de Almeida* apresenta um rasgão (aproximadamente 4.0cm por 2.3cm) juntamente com perdas das camadas pictóricas no canto superior direito, onde é possível observar uma camada de encolagem com uma espessura fora do vulgar (aproximadamente 50 mícrons) e a tela de trama invulgarmente aberta. As camadas de encolagem, feitas de cola animal, por serem susceptíveis às flutuações de humidade relativa (HR), poderão sofrer graves alterações dimensionais e, assim, afectar a estabilidade da pintura. Neste caso, a resposta à HR da camada de encolagem é mínima e a pintura apresenta-se pouco fissurada e quase sem destacamento. Isto sugere que a camada de encolagem sofreu pré-tratamento para a tornar insensível à humidade ou água. Reconstruções baseadas em receitas do final do século XIX, usando materiais historicamente apropriados, foram preparadas com o objectivo de explorar várias opções que possam tornar a camada de encolagem não higroscópica e, ainda, com o intuito de identificar o processo que foi utilizado no Retrato.

A tese é apresentada em duas partes:

Parte 1: Descreve a história, condição, materiais e técnicas da pintura. De igual modo, detalha o tratamento de *Januário Correia de Almeida* assim como as escolhas feitas e problemas encontrados durante o tratamento.

Parte 2: Aborda a história da produção de gelatina comercial, a escolha da origem animal apropriada para extrair o colagénio a utilizar nas reconstruções da camada de encolagem do retrato, assim como a caracterização de reconstruções seleccionadas.

A execução de um preenchimento superficial texturado resultou numa publicação e uma apresentação:

Resumo aceite para apresentação e publicação em *International Meeting on Retouching of Cultural Heritage* (RECH3), Francisco Brites, Leslie Carlyle and Raquel Marques, ‘’Hand building a Low Profile Textured Fill for a Large Loss’’.

Palavras-Chave: tela de trama aberta; camada de encolagem; gelatina comercial; Mowiol® 4-88; BEVA® 371b; reconstruções historicamente apropriadas.

ABSTRACT

This thesis project concentrated on both the study and treatment of an early 20th century male portrait in oil from Colecção Caixa Geral de Depósitos, Lisbon, Portugal. The portrait of *Januário Correia de Almeida*, exhibits a tear (approximately 4.0 cm by 2.3 cm) associated with paint loss on the right upper side, where it is possible to observe an unusually thick size layer (approximately 50 microns) and an open weave mesh canvas. Size layers made from animal glue remain subject to severe dimensional changes due to changes in relative humidity (RH), thereby affecting the stability of the painting. In this case, the response to moisture of the size layer is minimal and the painting is largely uncracked with very little active flaking. This suggests that the size layer has undergone pre-treatment to render it unresponsive to moisture or water. Reconstructions based on late nineteenth century recipes using historically appropriate materials are used to explore various options for modifying the characteristics of gelatine, some of which may relate to the Portrait's size layer.

The thesis is separated into two parts:

Part 1: Describes the history, condition, materials and techniques of the painting. It also details the treatment of *Januário Correia de Almeida* as well as the choices made and problems encountered during the treatment.

Part 2: Discusses the history of commercial gelatine production, the choice of the appropriate animal source to extract the collagen to produce reconstructions of the portrait's size layer as well as the characterization of selected reconstructions.

The execution of a shallow textured infill led to one publication and one presentation:

Abstract accepted for presentation and publication, *International Meeting on Retouching of Cultural Heritage* (RECH3), Francisco Brites, Leslie Carlyle and Raquel Marques, ''Hand building a Low Profile Textured Fill for a Large Loss''.

Keywords: mesh canvas; size layer; commercial gelatine; Mowiol® 4-88; BEVA® 371b; historically accurate reconstructions.

SYMBOLS and ACRONYMS

µ-	Micro
®	Registered Trademark
DCR	Departamento Conservação e Restauro
EDX	Energy Dispersive X-Ray
EDXRF	Energy Dispersive X-Ray Fluorescence
FCT	Faculdade de Ciências e Tecnologia
FTIR	Fourier Transform Infrared Spectroscopy
HART	Historically Accurate Reconstruction Techniques
IR	Infrared
MW	Molecular Weight
OM	Optical Microscopy
PVAL	Polyvinyl Alcohol
Py-GC/MS	Pyrolysis-Gas Chromatography-Mass Spectrometry
RH	Relative Humidity
RSG	Rabbit Skin Glue
SEM	Scanning Electron Microscopy
UV	Ultraviolet

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PART 1- STUDY OF THE MATERIALS, TECHNIQUES AND TREATMENT OF THE PAINTING

1. INTRODUCTION

This thesis focuses on the male portrait in oil of *Conde de S. Januário* along with its treatment and a study of its materials and techniques (Part 1) as well as a detailed investigation of the size layer (Part 2). The painting presents an unusually thick size layer on an open weave canvas. Normally a painting with such a thick size layer should have on-going problems with paint flaking and overall dimensional stability, related to RH response, since animal glue undergoes severe dimensional changes which the paint composite cannot follow and which affects the planar stability of the painting [4]. However in this case flaking is minimal and isolated samples of the size layer indicate very little response to water suggesting that this layer has undergone some form of treatment to remove its RH sensitivity.

In Part 2, reconstructions based on late nineteenth century recipes explore various options for modifying the characteristics of gelatine with the hope of identifying the process used on the painting to create the insoluble collagen-based size layer [5]. A better understanding of the size layer was important in the design and application of the treatment, in particular the tear and the missing paint.

1.1. Description of the Painting

This official portrait from the early twentieth century (oil on canvas), by Pinto da Cunha, belongs to Colecção Caixa Geral de Depósitos, Lisbon, Portugal. The man portrayed is ''Conde de S. Januário, Presidente do Conselho Fiscal (1881-1900)'' [1] (Fig.1). The figure is in the foreground and centered in an undefined background. He is presented in a formal position wearing his military uniform, the details of which are of great importance since they display his status and his awards placing him at the top of the hierarchical pyramid as a social and military leader [2]. The basic upper features of the uniform, namely the dolman (military coat) and the collar, identifies this uniform as one used between 1885 and 1892 in Portugal [7]. The dolman is made of blue cloth with two gold metal buttons visible. The collar is opened with rounded corners and made from red cloth containing also gold ornaments. As for the epaulettes (ornamental shoulder pieces), these are of gold metal with six scales (that can be related to its hierarchical position), laid on red cloth. Lastly there is a gold aiguillette (ornamental braided cord) placed on the sitter's right shoulder.

Figure 1- *Conde de S. Januário* portrait, normal light, photograph before treatment.

1.2. Historical Context

According to Saraiva, the development of art in Portugal was affected by general alterations in society and the impoverished economy, until the triumph of the Liberal army in 1820 [8]. Until then neither the government nor the church could invest in new structures. In the first twenty years of Liberalism, which lasts until the Regeneration (1834-1851) - art in Portugal presented a revivalist style, i.e. exhibiting mixtures of traditional and modern styles (especially in architecture) that lasted until the beginning of the twentieth century [8,9].

The economic growth in the last quarter of the 19th century, allowed the development of artists, most specifically portrait painters, since the Bourgeoisie society created capacity, ordering self-portraits from artists [8]. Thus, as José Mattoso notes, the portrait in Portugal became very common, as the Bourgeoisies desired to exhibit their social and political status [10].

1.3. Januário Correia de Almeida (1829-1901)

According Zûquete, writing in 1989, the sitter, Januário Correia de Almeida was in the military, a colonial governor, a politician and a Portuguese diplomat. He was the 1st Baron, Viscount and Earl of São Januário, who was born in Paço de Arcos, Oeiras, Portugal (March 31, 1829) and died on May 27, 1901. He enlisted in the *Caçadores* (Hunters), term which is used to designate light infantry soldiers, on November 4, 1842, and after attending Army School was promoted to second Lieutenant of cavalry on March 22, 1846. He subsequently went to the University of Coimbra where he studied in Mathematics and Philosophy then returned to the Army School, graduating as a Lieutenant and joining General Staff in 1856 [2].

On the General Staff, he followed his military career and was promoted to Captain in 1863; to Major in 1876; to Lieutenant Colonel in 1879; Colonel in 1884; Brigadier General in 1893 and to Major General in 1896.

Januário reached the top position in The Army and with that came important positions in Portuguese society, for example in 1880 where he was named Peer of the Realm, and was also Councillor of State and Aide de Camp of King D.Luís. By 1896 he was delegated to the command of the 1st Military Division and was also commander of the General Staff and the Military School [2].

1.4. Costume and Awards

As noted by Zûquete, Januário Correia de Almeida won several decorations and some can be identified in the painting and which represent rewards by the Head of State for services rendered to the country. These awards are for, boldness, courage, bravery, selflessness and other personal, civic and military virtues and are detailed in Appendix III [6].

2. CONDITION REPORT

In general the portrait did not initially appear unstable, since the significant paint loss associated with the tear on the upper right side was due to a single incident. However, the image was not acceptable for display due to a thick layer of dust and dirt (Fig.I.3) and because of the paint loss which exhibited active flaking, both at the interface of ground and canvas and at the interface of paint and ground (Fig.II.3). The missing area of paint associated with the tear is approximately 4.0 cm long by 2.3 cm wide.

2.1. Auxiliary Support: Stretcher

The auxiliary support (wooden stretcher or strainer) has the main function of holding the canvas under tension by keeping it taut and in plane [14]. In this case, the auxiliary support is a wooden stretcher (likely softwood) which measures 65 cm x 54 cm, with a Blind Mortise & Tenon corner construction (2 wooden keys with 2 blind slots) [14]. The stretcher has a horizontal cross bar in the center and all 9 keys are present. The wood is sound although it has some small splits and the corners are slightly distorted from square. There are also two exit holes from a previous insect infestation on the bottom part of the stretcher (Fig.II.1).

2.2. Original Support: Fabric

The portrait is painted on a single piece of wide mesh[1] plain fabric with a fine thread. Fibre identification indicated bast fibres, likely linen (see Appendix V.4). The thread count consisted of 12 vertical and 10 horizontal threads per cm^2 (The Baxter Method for Thread Counting was used to compare thread counts from this and other paintings. Threads are photographed through a $1cm^2$ square window of graph paper, which allows threads to be counted on an enlarged digital image, see Fig.II.2). The canvas and the size layer could be clearly observed in the area of paint loss associated with the tear at the top right (Fig.II.3). Such plain woven mesh canvases with thin individual threads and a low thread count are reported to be common in paintings from latter half of the nineteenth century in France[2] [53]. Townsend reports their use by Turner (approximately 10-12 threads per cm^2) between 1830's – 1840's in the UK [12]. Similar wide mesh canvases are seen in the 17th century Italian paintings[3]. Kate Seymour, SRAL, Maastricht, NL, notes that in Italy these canvases are referred to as *pavemento canvases*.

The back of the canvas bear the stencil marks, ''F'' and ''15'' which corresponds to a table of standard stretchers with prepared supports from the firm of *Bourgeois aîné*, that was published in a catalogue from 1888 (it was reproduced on page 46 in the *Impressionism: Art in the Making* catalogue from the National Gallery London Exhibition (1991) [11]. The portrait corresponds exactly to the dimensions for ''15 F'' in the table. The number 15 refers to the standard size (65 x 54 cm) and the letter F to the word ''*Figure*'' (Fig.II.4). While it is not possible to date the support precisely, the stencil and the corner construction (mentioned above) place it after 1888 as stated by Labreuche. According

[1] Mesh- any fabric, knitted or woven, with an open texture, fine or coarse. Described by Dan River, in his book, *A Dictionary of textile terms* (1980, 13th edition, page 63).
[2] Personal communication from Anne Baxter, Paintings Conservator, Montpellier, France, August 2015.
[3] Personal communication from Leslie Carlyle, based on observations of 17th century Italian paintings in the Exhibition, ''L' Age d-Or de la Peinture à Naples, Musée Fabre, Montpellier, France, August 2015.

to Labreuche this type of stretcher appeared first in the 1888 catalogue (*Janvier 1888. Catalogue general illustré. Fabrique de Couleurs Fines* […] *Bourgeois Aîné* […], (pg.86)) [13].

2.3. Sizing and Preparation Layers

A painting is a multilayered structure made of composite materials [14]. Traditionally, the first layer applied onto the support is the size, with the main function of isolating the canvas to reduce its absorption, and to ensure that the ground or preparation layers do not penetrate to the back of the canvas through the fabric interstices [14,15,16]. According to Witlox [16], who researched ground preparation in Northern Europe from 1550-1900, the most commonly used material for canvas sizing was animal glue, although other materials might have been employed, such as starch or flour paste sizes [15, 16]. As noted by some authors [4,16,17,18] size layers are often too thin to be readily visible on a painting and in cross-section. Nevertheless that is not the case for this portrait since it presents a very thick size layer especially relative to reconstructions from the HART Project (see Appendix VII.1).

Studies carried out by Mecklenburg demonstrate that an animal glue size layer is more flexible in high RH but very rigid at low RH and is the material in a canvas paintings that develops the greatest stress when desiccated while the painting is under tension (stretched on a stretcher/strainer) [4]. Hence Mecklenburg proposed that this layer could be responsible for the stresses that cause rupture (cracks) in the paint composite system at low RH. An especially thick size layer of untreated collagen (glue) would be expected to also cause delamination since at very high RH the glue size has no strength while the canvas shrinks. As the glue loses its adhesive qualities (while swelling and changing in dimension) the ground layers (and paint) can detach from the canvas.

The Portrait's size layer was analyzed by μ-FTIR, confirming the presence of a protein based material (most likely collagen). This proteinaceous material is extensively described in Chapter 5.

The preparation layers (also called the ground) are applied after the size and can have many functions, but primarily provide a surface for the application of paint. The preparation layers play an important role in the overall texture of the painting since the fabric texture can either be reduced or enhanced and in addition this layer can vary in absorbency [15]. The ground has to make good bonding properties between the canvas and the paint layers otherwise there is a risk of delamination [15].

The portrait's ground is a light grey-beige colour and covers the canvas thinly and evenly making the fabric texture visible but not pronounced. In the x-radiograph its application is visible and appears to have been applied by brush (Fig.I.6). It is likely that the ground was commercially prepared since it extends evenly to the edges of the tacking margin. An indication that it was commercially prepared, as noted above, are the stencil marks on the canvas (section 2.2).

Overall the ground is in good condition, except for the tear area where paint and ground have suffered mechanical damages. Even within this large loss of both paint and ground, there are islands of intact ground and paint which appear to be well adhered. There are also very small (approximately 1 to 3mm) paint/ground losses elsewhere on the painting (Fig.II.5). It is unclear whether these are all due to the rough handling which resulted in the tear, or whether the painting also has a problem with flaking (Fig.IV.1). SEM images of the ground suggest the latter, as discussed below.

2.4. Pictorial Layers

The paint is very thinly applied, with semi-opaque paint, both in the dark and light colours. There are a few areas of impasto (more noticeable on the medals) and some textured brushstrokes in the background, yellow collar and the epaulettes. The layering application is very notable in the green sash, where both the layer of a light green (evident along the bottom edge) with a brownish top coat are visible; this is confirmed by the cross-section stratigraphy (Fig.V.4). However the sequence of the paint layers is difficult to define on the background, due to an overlap of different tonalities. In the lighter areas a yellow tone (left side of the background) is more pronounced with absence of the dark green (right side of the background). This visual appearance was also confirmed with one cross-section stratigraphy (see Fig.V.5).

Overall the painting presents both local and minor mechanical and drying cracks. The first type of cracks can be easily seen in the sitter's left cheek under the stereomicroscope (see Fig.II.6). As for the drying cracks these are confined to the black uniform, specifically between the junction of the neck and the collar (Fig.II.7 A and B). There are also abrasions along the edges that are associated with the frame (see Fig.IV.1).

2.5. Surface Coating: Varnish

Normally the varnish is the last coat to be applied to a painting for the purpose of saturating the colours as well as evening out gloss [15].

The painting clearly shows varnish coatings visible both in normal and Ultraviolet (UV) light, which are best seen on the bottom edge of the sash (Fig.I.4). Under UV light, the surface presents several peculiarities, since there are two types of fluorescence': one greenish (near the shoulder's and background) and a blueish tone (located over all of the black uniform and medals), suggesting the presence of a natural resin (Fig.II.9) [14]. The sash and the sitter's right side show an opaque dark coating (Fig.II.8). Cross section S8 reveals the presence of a thin varnish layer, although S6 which corresponds to the sash, does not fluoresce and exhibits the same dark opaque tonality.

Although no analyses were carried to characterize the varnishes, it is suggested that the surface of the painting has a retouching varnish. According to Carlyle, retouching involved applying over a previously painted passage a layer or layers of ''retouch varnish''. It was recommended when the paint had become dull or there was a lack of medium at the surface [15]. As noted by Carlyle, by the end of the 19th century retouch varnish was likely to consist of a fast drying solvent-based varnish, such as shellac in alcohol [15,19].

Overall the varnish applications are very uneven and the coating is transparent yellow (more evident in lighter areas, such as the background and flesh tones). The varnish coating stops at the bottom and the left frame edge (Fig.II.8) and there are signs of drips above the head as well as the sitter's right shoulder (near the background) (Fig.II.11). In addition, the surface is covered with a thick layer of dirt, which also lowers the surface gloss and distorts the colours.

3. CHARACTERIZATION OF MATERIALS AND TECHNIQUES

3.1. Painting Technique

The paint is applied in layers which are similar to those described in instruction manuals on oil painting, in Britain, France and Portugal from the mid eighteenth century and throughout the 19th century [14,19]. Such system required the paint to be applied in separate stages with the paint being allowed to dry between each layer [19,20].

The areas where the technique is most pronounced is in the forehead, the eyes and the background. The forehead exhibits two tonalities of beige (one lighter than the other) over which red, brown and white shades are used to build the following features: cheeks, nose, eyes, eyelids and chin (Fig.II.10). As for the background this presents a green brown tonality, although there is a shift in hue, since there are more pronounced tones of blue and yellow in the right side as well as more red and yellow shades in the left side (Fig.II.11).It is also possible to observe layers made with mixtures of different pigments as well as impasto paint which is most evident in the medals.

By comparing the X-radiograph with the paint under normal light, a difference was detected between the sitter's right eye. On the X-radiograph a misalignment and deformation are visible (see Fig.I.6). This suggests that the artist decided to change the appearance rather than an overpaint done by another artist, since the technique, colour palette and brushstrokes are extremely similar with the rest of the painting.

To confirm the layer stratigraphy, cross-sections were mounted and most indicate the presence of two paint layers, although in one case, in the background (S8, see Appendix V.3, Fig.V.5) a third layer was visible. There are no signs of restoration layers on the cross-sections analysed, nor was there evidence of restoration on the painting over all.

3.2. Analysis of Materials

The paint was analysed by µ-EDXRF and cross-sections were examined by OM, SEM and µ-Raman, while micro samples were analysed by µ-FTIR. For more complete information regarding the pigments identified in the ground and paint layers see Appendix V.5, Table V.2 and V.3.

The size layer information and analysis are fully detailed in PART 2.

Concerning the preparation layers on the portrait, under the OM it was possible to observe in most cross-sections a beige ground. Sample S4 contains the size layer alone (see Fig.V.2, V.3). SEM provided information on the morphology and on the stratigraphy of the ground (S5) and size (S4). The sample with the ground and size layers (S5) (Fig.2A) exhibits a sign of extreme instability: at the interface between the ground and size layer is a line of detachment. The sample with size alone, S4 (Fig.2B), where the paint/ground had previously been lost shows a top surface the same as the top surface of the size seen in S5. While cross-sections can show delaminations and damage due to sampling, the presence of the line of delamination in S5 and the evidence that the ground had delaminated in the same place in S4 suggests that the delamination line in S5 is a characteristic of the painting, and not just sample damage. To confirm this, more sampling of the ground and size layers would be necessary from different locations, since one sample might not be representative.

EDX analysis of the ground (S5) shows mainly Lead (Pb), Barium (Ba) and Sulphur (S). Zinc (Zn), Calcium (Ca), Phosphorus (P) and Fluorine (F) are also present. The Zinc (Zn) associated with

Sulphur (S) suggests the addition of zinc sulphide (ZnS). The Calcium (Ca) and Phosphorus (P) suggest the presence of calcium phosphate ($CaPO_4$). As for the Fluorine (F) it is associated with Calcium (Ca) and indicates the presence of fluorite (CaF_2). The Calcium (Ca) and the association with Sulphur (S) suggests the presence of gypsum (calcium sulphate dehydrate, $CaSO_4.2H_2O$). However, the analysis by µ-Raman of the ground in cross-section S6 showed evidence of only barium sulphate ($BaSO_4$) and lead white ($2PbCO_3.Pb(OH)_2$) (see Table V.2), possibly because the signal of barium sulphate and lead white overwhelm the signal of the other compounds present in very low amounts. These results are in accordance with the results from µ-FTIR, which indicated only the presence of barium sulphate and lead white in S6. The presence of fluorite particles could be associated with the Barium Sulphate as an impurity [54]. The binder present in the ground was identified as a drying oil by µ-FTIR (Appendix V.6). The appearance of the ground in OM strongly suggests a homogeneous layer (Fig.V.3, V.5).

The materials identified in the paint layers are: lead white, carbon-based pigment (carbon black), chrome yellow, vermilion, ultramarine blue (likely artificial ultramarine). The µ-FTIR spectra of the green identifies the presence of a copper carboxylate [47]. Chromate anion, CrO_4^{2-}, is also present. By combining the information of µ-FTIR and µ-EDXRF (Appendix V.5, Table V.3), possibly the green is composed of a mixture of a copper based pigment and chrome yellow. All are consistent with the period of the painting.

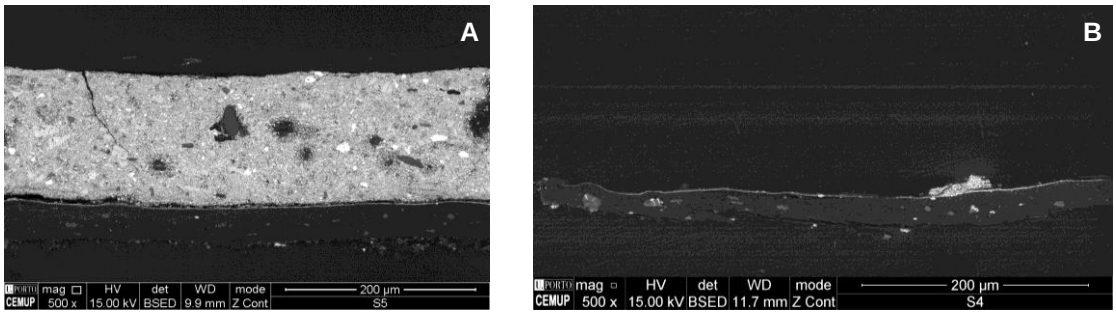

Figure 2 – SEM images. (A) is sample S5, ground and size, and (B) is sample S4, size alone. Image (B) suggests the delamination zone at the interface of ground and size.

4. TREATMENT SUMMARY

4.1. Surface Cleaning

As noted in Chapter 2, the painting presented a very thick layer of dirt, which was hindering the overall reading of the painting since most of the colours were very dull (see Figure I.3, Appendix I). Cleaning is normally undertaken to recover the general appearance of the painting [14]. To improve colours saturation and aesthetic value, surface cleaning was performed in two stages using aqueous materials. First with distilled water, which removed a significant amount of dirt, then saliva was used (Fig. 3). This second step was undertaken, since it was noticed that after an overall cleaning with distilled water, while no further dirt was being removed (according to the cotton swabs) the surface still exhibited a dirt layer obscuring the paint surface. This remaining layer was easily removed with saliva. A final rinse with distilled water was done after cleaning the surface with saliva. After this stage, the colours emerged brighter and richer (see Fig.VI.1).

Figure 3 - Before (left) and after (right) surface cleaning images of a medal.

4.2. Consolidation

Consolidation can be defined as the action used to re-adhere materials that previously have lost their ability to bond [14].

As noted in Chapter 2, the portrait suffered severe mechanical damage that resulted in a tear associated with paint and ground losses. To prevent more flaking in this area, consolidation was performed to secure the paint/ground layers at the edges of the previous losses as well as minor losses in other areas (approximately 1 to 3mm size) using BEVA® 371b[4] (BEVA). This adhesive is a mixture based on poly(ethylene-vinyl acetate) (EVA) copolymers that is known for its high tack, strength, and elasticity/flexibility [14,21]. BEVA is also a "heat-seal" adhesive that is soluble in petroleum distillate solvents (white spirits, naphtha and toluene) [21].

Using a small brush (Winsor & Newton No.00) a BEVA solution of approximately 1:1 in white spirits (this dilution achieved the desired flow properties) was introduced locally. The adhesive penetrated easily into cracks and underneath the paint and paint composite. The operation was performed under a magnifying microscope. After the BEVA had dried somewhat (approximately 15 minutes), the

[4] BEVA® 371b adhesive was originally designated BEVA® 371, which contained two EVA copolymers (Elvax 150 (45%), A-C 400 Copolymer (15%)), a ketone resin tackifier (Laropal K80 (27%)), a phthalate ester plasticizer (Cellolyn 21 (4%)) and a paraffin wax (9%) [22,23,24]. As reported (http://www.conservationsupportsystems.com/system/assets/msds/New_Beva_Formula), the reformulated BEVA® contains an aldehyde ketone resin to replace the former Laropal K80.

consolidated paint, covered with a silicone coated polyester film (Melinex®, see Suppliers) was pressed down gently with a heat spatula set to approximately 65ºC (see Equipment). Immediately after heating, while the paint composite was still plasticised, two light lead weights (each 237.2g) were applied over the areas consolidated to flatten the paint and while the adhesive set (Fig.4).

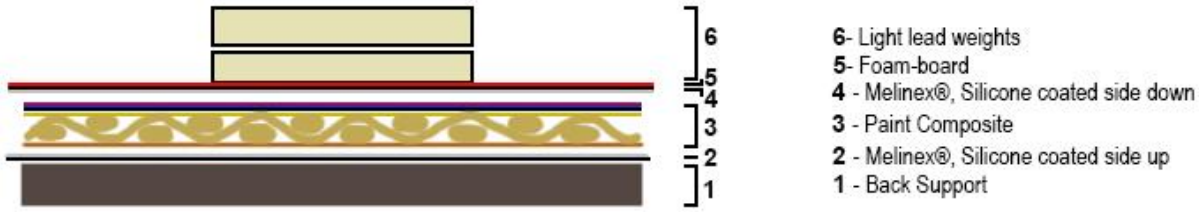

Figure 4 – Diagram of the system used during consolidation.

4.3. Tear Repair

As explained by Tomkiewicz, in *Conservation of Easel Paintings*, p.384, tear mending aims for maximum recovery of the condition prior to damage by returning similar stress tolerance and flexibility to the damaged area as well as to recover the weave pattern, thread count and thread distance [14].

Prior to tear repair, in order to support the individual threads and effect their alignment on either side of the tear, a small raised lump of plasticine (see Suppliers) covered with thin Melinex® (25 microns) was placed underneath the painting, immediately below the affected area. This plasticine sat on top of a board which was placed beneath the painting. To ensure good alignment and easy manoeuvrability of the fibres, a piece of blotting paper (4cm long by 1,5cm wide), previously moistened with distilled water, was suspended over an area which covered approximately 14 threads at once (see Fig.VI.2). The blotting paper was left in place for approximately 10 minutes. This moisture treatment allowed the fibres to relax. Threads were then lined up across from each other, this realignment was aided by the raised plasticine as it conformed to the distortion in the threads (Fig.VI.3). The threads were then joined under 10x magnification (using optivisors, see Suppliers), by applying with a brush a drop of 40% solution of Paraloid® B-72[5] (B-72) in xylene to both thread ends and creating a slight overlap in the centre (butt join with slight overlap). B-72, an acrylic resin, presented good tensile strength and flexibility, enough to hold the threads together since the canvas would not be under significant further tension (the painting was still in its original stretcher and was at the correct taughtness) (see Fig.VI.4). According to Horie, B-72 does not degrade significantly in normal conditions of exposure, although oxidation can occur slowly [24]. This acrylic polymer is considered one of the most stable resins available for conservation use [14,24]. After the realignment of the threads, when the B-72 was fully dry (after a week) a local flattening of the whole area around the torn fabric was carried in order to ensure that the paint surface was completely in plane before applying the fill (see Fig.5).

[5] Paraloid® B-72 is a copolymer of ethyl methacrylate and methyl acrylate (EMA/MA, 70/30 proportion) [24].

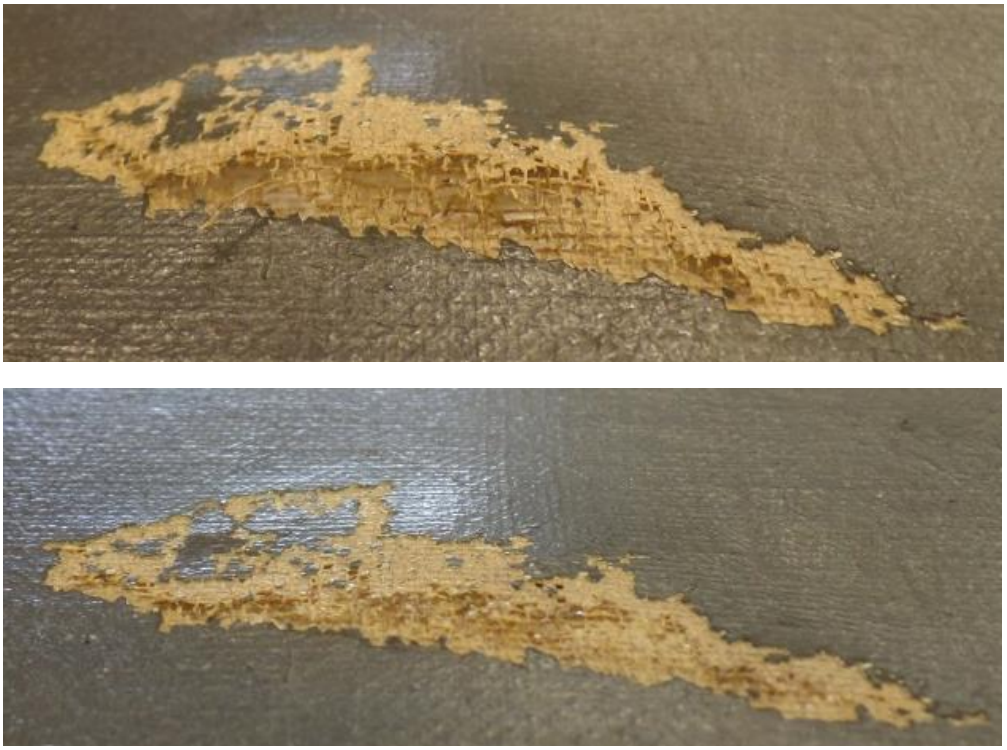

Figure 5 - Before (top) and after (bottom) tear repair treatment.

4.4. Local Flattening

The back of the painting was supported with layers of boards, the one which sat next to the canvas cardboard was covered with silicone coated Melinex®, facing up. This then allowed an even distribution of boards and cushioning materials with weights that were going to be applied from the top as well as providing a flat surface during flattening.

Prior to flattening, the canvas and paint composite required plasticising with moisture. Blotting paper was pre-moistened[6] then cut to the size of the distorted area. Dry blotters larger than the moist blotters were placed over the top. Once in place the blotters were covered with thin Melinex® (25 microns) to prevent moisture loss. Beneath the blotters it was placed silicone coated Melinex® (side down) with rounded edges to prevent direct contact of the paper with the painting (see Fig.VI.5). The moisture response of the painting was constantly monitored with gentle finger pressure until the canvas/ground/paint became flexible. It was established that 10 minutes was the most suitable length of time. Once plasticity was achieved, the blotter was removed and rapidly replaced with light lead weights on top of silicone coated Melinex® (facing down) (Fig.VI.7). Gradually as the distortions were reduced, light weights were replaced by a large flat lead weight supported on a piece of foam-core to better achieve a plain surface (Fig.VI.6). This process was repeated until complete flattening was attained.

[6] Previously sprayed with distilled water then sealed in Melinex® with weights on top for 10mins before use to allow a good moisture distribution within the blotter.

4.5. Infill: texture fill

In order to improve the physical and aesthetic values in the area of the large loss, 2 stage infilling was undertaken. The choice of materials are carefully made and based on what was most appropriate for this painting and the size and thickness of the lost paint/ground. Due to the loss of the size layer between the threads it was important to guarantee that before introducing the filler in the lacunae, to avoid having the filler run through to the back of the canvas, an infill material was needed which could be capable of being as thin as the size layer, as well as flexible and stable. The system that best suited these requirements is used in SRAL[7], it consists of a mixture of BEVA®371b and kaolin[8] (Fig.VI.8). It forms a flexible infill material. The filler also exhibits a tonality very similar to the size layer present in the painting. A strip was cut from a thin film of this mixture and was heated between sheets of thin silicone coated Melinex® with a heat spatula to create a thinner film close in thickness of the size layer (see Fig.VI.9). From this very thin fill, small squares were cut in order to insert the film between the threads to fill the gap left by missing size. By heating a dental tool and placing silicone coated Melinex® (side down) on top of the filler, the fill material was inserted such that it bridged the gap between the threads while some of it was incorporated into the canvas threads so that it was secure (Fig.6). This operation was carried until no more gaps were found.

Figure 6- Appearance of damaged area after BEVA®371 + Kaolin fill material was applied.

The second stage of infilling involved the execution of a shallow textured infill. In order to prepare for reintegration, the topography of the infill needed to match its surroundings. Initial attempts to cast a silicone mould of the surface texture were frustrated because the painting remains on its original stretcher, therefore achieving conformation of a barrier film against silicone staining by using the low-pressure suction table was not possible. Given the very low profile of the original paint texture, it was necessary to find a material which could provide an extremely thin textured film but that would remain flexible. According to Devesa, who studied several binders and fillers for her Master's Thesis [18], Mowiol® 4-88 (Mowiol) exhibited good working properties and did not form severe cracks as it has very low shrinkage [18]. According to Horie, this polyvinyl alcohol (PVAL) material, which is soluble in water, is very stable to oxygen/ultraviolet ageing since chain scissions occur very slowly, but he notes

[7] This method was developed at the Stichting Restauratie Atelier Limburg (SRAL), Maastricht. In 2013 Kate Seymour, Head of Education at SRAL, provided a workshop at DCR-UNL to instruct on the use of this method. It was originally developed by SRAL's senior painting conservator, Jos van Och.
[8] 10gr BEVA®371 + 7.5gr Kaolin. The proportion depends on the properties desired for the filling material.

that it might become insoluble if in acid or alkaline conditions. Therefore, Horie states that treatments done with Mowiol are irreversible. However, the irreversibility of this binder is not a main concern since it does not cover original paint and can be removed mechanically. Although water based in application, Mowiol® 4-88 does not affect the size layer, as it would in a normal painting. 20% Mowiol®4-88 in distilled water (10g Mowiol to 50 ml water), was mixed with Champagne chalk (natural calcium carbonate from France, see Suppliers), until the desired properties (the more chalk is added to the Mowiol, the greater the viscosity). Mowiol itself has excellent working properties and is very easy to manipulate. The working time is also very good, since it easily allows alterations while it is being applied.

Tests with the mixture applied in thin films to Melinex® (25 microns) and allowed to dry, showed that on bending the Melinex®, the fill material easily cracked. However, when a brush coat of BEVA (60:40 in white spirits) was applied to the dried film, and then allowed to dry itself, the combination of the Mowiol and BEVA was very flexible, showing no signs of cracking when bent. A further advantage to saturating the Mowiol infill with BEVA is that is likely to reduce the Mowiol's response to humidity (Horie notes that it is hygroscopic, since it will absorb water vapours above 75% RH [24]).

The infill was initially applied in a thin film with a brush and allowed to dry (Fig.VI.10). This step was repeated until the desired thickness was achieved. Applying water-based infill materials in a series of thin layers which are dried in between coating, ensures that the material does not crack during application. To smooth the rough surface of the infill, a cork covered with a thin polyester net fabric was moistened then rubbed over the surface (Fig.VI.11). All these actions were done using an optivisor and raking light, since it was necessary to pay careful attention to shadows to detect any missing infill material.

To achieve a textured surface matching the surrounding paint, tiny dots and lines were laid over the infill. Reference points (like fine brushstrokes) were chosen and used to recreate the lines with the fill material, in order to mislead the eye and accomplish the final textured surface prior to reintegration. As noted above due to the need for this thin fill to be flexible over a relatively large surface area, the infill was plasticized with an infusion of Beva®371b in white spirits to prevent it from cracking. To achieve a closer texture to the original, the infill material was softened (see Fig.VI.12 before softened) with a moistened cotton micro-swab. By gently rubbing the surface of the Mowiol, it gradually achieved the topography of the original surface (Fig.7).

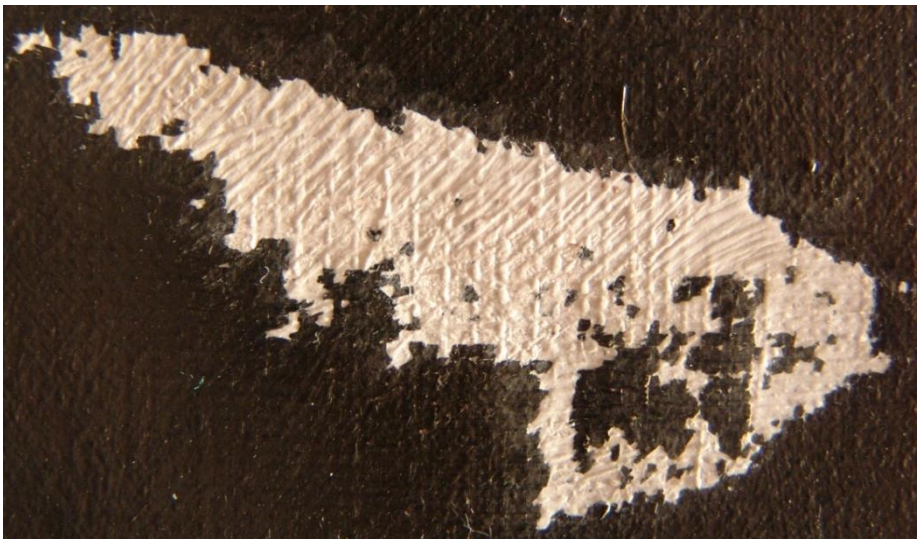

Figure 7 – Final appearance (after softened) of textured fill under raking light.

PART 2- INVESTIGATION OF THE SIZE LAYER

5. HISTORICALLY APPROPRIATE RECONSTRUCTIONS

To better understand the art of the past, a methodology has been devised with the aim to recreate historic oil painting materials with as much accuracy as possible by exploring historical recipes [17]. Reconstructions help interpret historical recipes since we can learn why materials were prepared in a certain way and if a correlation can be established with an actual sample from an oil painting. If made from historically appropriate materials results from reconstructing recipes can be used as reference material for visual and chemical analysis. Furthermore the effectiveness or performance of the materials can be evaluated during use and their chemistry explored [16,25,26,42]. Reconstructions can be made to answer particular questions in conservation research and can therefore be modelled to look at specific ingredients and their effects [25,26]. For reconstructions aiming at a degree of historical accuracy it is important to note that modern materials are unlikely to have exactly the same physical characteristics and chemical composition as those used in the past. An investigation is necessary to understand how modern materials may differ from the materials that would have been used in the period contemporary with the recipe(s) chosen [25,26,42].

Because of the unusually thick size layer on the portrait, and the lack of response of this layer to RH changes, as well as the use of the open weave fabric (mesh fabric), an investigation was undertaken with historically appropriate reconstructions based on a series of gelatine size recipes in the painting instruction manual by Jehan Georges Vibert (*The Science of Painting*- A translation from the eighth edition. London: Percy Young, 137, Gower Street, W.C) which was published in 1892 (pages 189-190). As noted by Carlyle, Jehan Georges Vibert trained at the École des Beaux-Arts and was awarded in 1864 with the ‘’medaille de Salon’’ [15]. Vibert’s recipes were chosen because he wrote extensively on artists’ materials at a time appropriate to the time of the portrait (his work was published only 9 year before the portrait is dated), and in addition Vibert produced retail products under his name: ‘’All the new productions spoken of in this book may be found in the house of Lefranc &Co., 64 & 66, Rue de Turenne, Paris (pg.196)’’ [5].

Some of Vibert’s gelatine size recipes were intended to modify the characteristics of the gelatine. Therefore by recreating the recipes, a series of reference samples would be available for studying those new characteristics and would allow a comparison with the portrait’s size layer offering the possibility of uncovering the method used for the gelatine in the portrait’s layer, as well as to explore ways of overcoming the challenges faced when interpreting old and vague recipes.

Reconstructions, using known amounts of ingredients in stepped proportions would also establish the detection limits of the instruments used for analysis. It was anticipated that reagents could be effective in rendering the gelatine unresponsive to moisture in amounts well below the detections limits of some instruments. By re-creating the recipes, the effect of the various reagents could also be determined during use.

As noted above, size layers in the past were commonly made from animal glues [16] although other size substitutes could be used such as starch-based sizes [15]. For this reason, it is important to know what types of materials were used during the period of the portrait under study. The choice of the raw materials for the reconstructions depended on discovering what materials were used and

appropriate for the time of the recipe. Evidence was found that a common gelatine source in use now, made from pigskin, was introduced in the 1930's [27] while 19th century references indicate that commercial gelatine came from bovine sources [48]. Furthermore as Schrieber notes, modern commercially prepared gelatines are not processed according to the same methods as used in the 19th [27]. Nowadays, the first step to produce gelatine is to reduce the raw material, by cutting or grinding. The bones are ground to between 2 to 25mm, while skins are reduced to 30-150mm. Degreased bone (called ossein) is then treated with hydrochloric acid. By the end of this operation, only organic matter remains [33]. Consequently reconstructions made with current commercially available gelatines do not represent the materials and processes used in the past, leading to the introduction of anachronistic variables. According to Schellmann, the information given by the suppliers is not reliable, and the exact composition of industrially produced collagen is difficult to know, since manufacturers tend to keep their recipes a secret [37]. In addition, Schriber notes that in making instant gelatine additives, such as carbohydrates (sugar, starch or maltodextrin) are used. As well, flavour and colour might also be added [27].

In contrast, Ure writing in 1840, notes that gelatine is an animal product that is obtained by boiling the muscles, skin, cartilages and membranes with water. Alcohol and tannin are used to precipitate gelatine from solution (but he states that no other acid, except the tannic is used and no alkali possesses the property of precipitating gelatine). He also notes that chlorine, nitrate and bi-chloride of mercury can render its solution more or less turbid, which implies that these materials were also used (pg.570) [49].

5.1. Size layer- Characterization and Analysis

As noted above, the size layer on the portrait exhibits unique characteristics. To gain more knowledge about this layer, a visual comparison under OM was done with a HART Project reconstruction and with samples of rabbit skin glue (RSG) 7% in water. Typically according to studies by Mecklenburg, a size layer has a thickness of 0.015mm (dependent also on the number of layers spread over canvas), however the size from the portrait has 3x greater thickness (approximately 50 microns) when compared to HART Project samples (which are approximately 13 microns). A size layer from another painting (*Landscape with Deer*), dated 1936, was also compared. The latter exhibits an identical morphology and thickness to the size layer from the portrait (see Appendix VII.1) [4].

To establish the portrait's size layer's sensitivity to relative humidity (RH) and water (that would help with the treatment as well as to know how it would influence the other composite layers), tests on isolated samples were carried out and compared with the response of three other size layers: a size of 7% rabbit skin glue (RSG) prepared in the laboratory; the size from a painting by Wassily Kandinsky (c.1900)[9]; and the size from an early 20th century oil painting, *Landscape with Deer*, with a similar mesh canvas and size layer to the Portrait. Micro samples were taken from the three sources and measured[10] prior to moisture and water exposure.

Moisture exposure involved placing the samples inside a polyethylene box (12cm x 8cm) for three days with two 10ml beakers filled with distilled water. A data logger was enclosed in the box to monitor

[9] From Art Acess & Research, London, UK. The author is grateful to Dr, Jilleen Nadolny for providing this sample.
[10] Measurements were performed with an AMX423X Dino-Eye Microscope Eyepiece Camera Software.

the RH to ensure 99%RH was attained[11] (Fig.8). Testing with liquid water was also carried out. This involved filling a 10ml beaker with distilled water and placing the sample in the water for a total of 15 minutes to allow a complete interaction with water. After the tests, the samples were all re-measured and compared to their dimensions before exposure (see Appendix VII.2).

Figure 8 – Plastic box used for RH tests, red circle shows size sample.

After both RH and water tests were completed (see Table VII.1, Appendix VII.2), it was possible to confirm the low RH and water response of the portrait's size. Of all the samples tested it was the least reactive (along with the Kandinsky size layer which was similar in behaviour to the portrait's size layer, although it cracked). Both the RSG 7% and the size from the *Landscape with Deer* exhibited considerable dimensional changes, especially in thickness, in the RH test, and dissolved completely in the water test.

µ-FTIR analysis on a reference sample of collagen (parchment glue) (**A**) and that taken from the portrait (**B**) showed that there were significant differences between the two (see Figure 9). Although the size from the portrait exhibits the common characteristics of a protein (Amide A, I, II and III) it also shows relevant particularities such as the regions (marked with a dot) at 1080cm^{-1}, which presents a higher absorption than the reference sample of collagen (parchment glue) (**A**) and at 1720 cm^{-1} a ''shoulder'' is displayed that might suggest the presence of shellac or other material with a similar absorption band. This is in agreement with the C-H absorption pattern observed (C-H stretching mode at 2939 cm^{-1}), which does not show a profile of a collagen type protein. The Amide A (designation given for amide infrared bands of proteins) is shown at 3300 cm^{-1} that corresponds to the N-H stretching mode. Consequently the Amide I is present at 1653 cm^{-1} (C=O stretching mode), the Amide II at 1547cm^{-1} (C-N-H bending) and the Amide III is seen at 1339 cm^{-1} (C-H bending mode) [28].

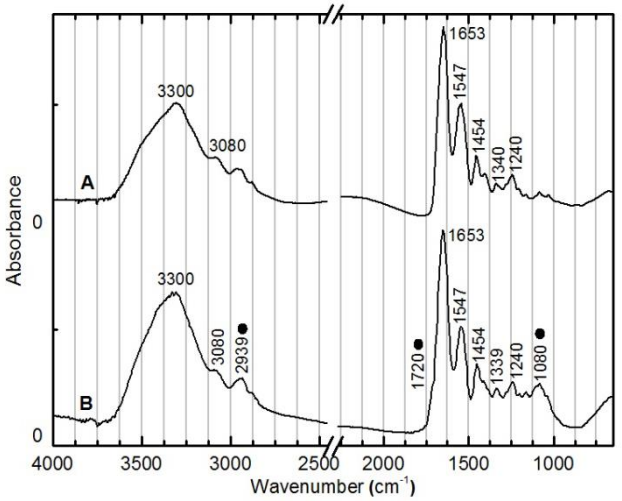

Figure 9 - µ-FTIR spectrum of the reference sample of collagen (**A**) and the portrait's size layer (**B**).

Given that the portrait size is non-responsive to RH and water when compared with a size that is responsive (as would be expected of an untreated size), and exhibited significant differences in µ-FTIR when compared with the reference sample, the supposition that the portrait size layer had been treated to render it non-hygroscopic was then considered in depth.

As mentioned previously, SEM analysis was carried in cross-section S4. EDX shows mainly Carbon (C), Sodium (Na), Calcium (Ca) and Chlorine (Cl). Potassium (K), Sulphur (S) and Lead (Pb) are also present. The Lead (Pb) is likely associated with the ground layer. The presence of Sodium

[11] Ambient conditions before tests were at 40% HR and 23ºC.

(Na) and Chlorine (Cl) could indicate the presence of sodium chloride (NaCl). Considering the substantial amount present, this could have been added as a flavouring agent (see identification of vanillin below which was also found in the size), and/or a preservative. However, as Dr Ure explains, soaking animal parts in brine prior to collagen extraction was also done (pg.895, Volume I) [49].

5.2. History of Gelatine

The use of gelatine has been traced as far back as the Ancient Egyptians [29]. However it wasn't until the 17th century that the French mathematician Denis Papin (1647-1712) recorded his research experiments on the subject, making it possible to cook bones by using a 'digester' (a pressure cooker) which he demonstrated to the Royal Society in London [30]. The main issue with making gelatine by this method was that it was a laborious process, since the bones had to be cooked under pressure for a full day (about 6-8 hours). The stock then had to be clarified as it dripped through a jelly bag and then boiled again prior to being finally been allowed to sit.

In 1754 the first English patent for the manufacture of gelatine was registered [31]. Methods of producing gelatine were systematically improved during the Napoleonic Wars since there was a shortage of meat protein for the population during this period and gelatine became an alternative.

In 1818 in Lyon, France the first company to manufacture gelatine on an industrial scale, Coignet & Cie., was established. Two types of material were used: the hide split (also known as 'glue leather') and gelatine leaves [27].

By 1842 The J and G Company of Edinburg, Scotland was producing dried gelatine and in 1845 the first American patent (US4084) for commercial gelatine was granted to Peter Cooper, called 'Improvement in The Preparation of Portable Gelatine'. It involved a dried product that just required the addition of hot water. The company mentioned above (J and G Company of Edinburgh) also began exporting its Cox Gelatine to the United States in the same year.

Aside from the food industry, new applications for gelatine were developed in both medicine and photography during the nineteenth century. Gelatine capsules for medicine began to be manufactured as early as 1833. In the field of photography, the British Journal of Photography announced the gelatine process in 1871 which had been developed by Richard Leach Maddox (1816-1902) [32].The use of gelatine provided a fast, sensitive photographic technique that further popularized photography since the negative plates could be sold ready-made [32].

As a modern product, gelatine has versatile range of uses (e.g. confectionary products, photography, and medicine) due to its multifunctional properties. According to Schriber, in *The Gelatine Handbook*, by the 1930's, the animal source in the manufacture of gelatine was pigskin. Previously it had been a bovine source, which did continue to be used after this time, but in much less quantity [27]. Another change was the conditioning method used. Nowadays, there are two types of pre-treatments: alkaline and acid. The alkaline treatment involves soaking in a 1% sodium hydroxide solution at 20ºC (this process can last up to 4 months), with supersaturated milk of lime. The sources [27,33] note that non-collagenous protein and other substances (which are not identified) are added. Regarding the acid pre-treatment, the collagen is soaked in a dilute solution (between 2-4%) of hydrochloric acid at room temperature, although phosphoric acid and organic acids (not specified) might also be used for this process [27]. According to Schriber, for the traditional extraction, drinking

quality water was used in batch processes where the gelatine was dissolved in different stages at temperatures between 50ºC and 100ºC. An interesting fact that Schriber notes is that gelatine colouration increases with increasing reaction time between protein and traces of carbohydrate in the raw material due to ‘’the Maillard Reaction (a reaction that takes place with amines and amino acids with reduced sugar content)’’(p.77). If colour is not wanted in the modern product then, oxidizing or reducing agents (e.g. hydrogen peroxide or sulphur dioxide) can render the product lighter [27]. Today there are a variety of production processes that result in gelatine with different properties [27].

5.3. Chemical composition and properties of gelatine

Gelatine is derived from collagen, which consists of protein molecules (amino acids monomeric units) that are linked by covalent peptide bonds and are the major structural protein found in skin, bone, tendons, cartilage and connective tissues. Gelatine is obtained by hydrolysis of the collagen [27,33]. This macromolecule exhibits different molecular structures: primary, secondary, tertiary and quaternary [27]. According to Osada et al, in 2000, the main peculiarity of collagen is its ability to crosslink by forming triple helixes caused by the formation of a helix by hydrogen bonding between the NH group of the prolin and the CO group of the peptide in hydroxyprolin [34]. It is also known that due to its triple helix collagen is insoluble in cold water but when heated, it loses all of its structure, since the triple helix unwinds and the chains separate (the H-bonds are broken). This process is called denaturation and thereby soluble gelatine is obtained [27,33,35]. Another relevant fact about collagen is that depending on the part of the animal from which it is extracted it will give different types of collagen [27].

This natural polymer exhibits properties that make it a unique biomaterial [27,36]. According to Schriber the main properties can be divided in two groups: gelling and surface properties [27]. The first group is concerned with the gel strength (or Bloom Value); gelling time; viscosity, setting or drying time and melting temperature while the surface effects are related to the adhesion/cohesion, film formation and emulsion. As stated by Schriber the Bloom Value is influenced by molecular weight but is also related to the degree of helical structure formation, since gelatine is an aggregate of polymeric chains. Viscosity is also dependent on the molecular weight distribution (the greater the proportion of molecules of higher MW, the higher it will be the viscosity) and varies widely [27]. The gelling time will rely on the prolin and hydroxyprolin amino acids content since the higher their content, the higher the MW: consequently a highly concentrated solution will have a slow drying time (which also develops into a more ordered network structure) [37,38]. Regarding the setting/drying time this characteristic is influenced also by the bloom strength, the gelling temperature, and as well the ambient temperature and relative humidity (RH). A low gelling and bloom value will mean that it takes longer for the gelatine to turn into a gel as (noted by Schriber) [27]. Schellman states that after the gelation the drying of the gelatine can be accelerated by increasing the ambient temperature [37]. Nevertheless such material should be allowed to dry as slowly as possible in order to have a highly ordered network structure according to Kozlov [38]. An ability of gelatine is its capacity to form colloidal solutions [27]. Gelatine also exhibits a characteristic that is very important: its reversibility, since when it cools, the solution converts into a gel, while if it is warmed it will turn into solution again [27].

The surface properties are based on the gelatine side chains that have charged groups and hydrophilic or hydrophobic amino acids as mentioned by Schriber [27]. These amino acids tend to migrate to the surface, thereby they reduce the surface tension of aqueous solutions. Another important property is the IEP (Isoelectric Point), since it will influence the overall charge distribution of the gelatine. Neutrally charged, the gelatine exhibits a ''random coil structure''. However, the pH of the matrix can shift and thereby change the charge of the molecule. With this, the molecule tends to unfold, thereby the pH will influence the surface effect of gelatine [27]. The binding properties of gelatine are based upon adhesion and cohesion. According to Schriber, adhesion is related to the interaction force between a solid interface and another substance, while cohesion is due to the interaction between the molecules within a substance [27]. When the gelatine solution has been spread over the surface, it will start to gel on cooling as the polymer cross links and returns to is helix form.

5.4. The terms glue and gelatine

The terms *glue* and *gelatine* are sometimes misunderstood. According to the Merriam Webster online Dictionary (accessed May 2015) the word *gelatine* is used to describe a glutinous material obtained from animal tissues by boiling[12]. As for *glue* this term refers to any of various strong adhesive substances especially a hard protein, chiefly a gelatinous substance that is obtained by cooking down collagenous materials[13]. To understand better the terminology for each term, Portuguese and French Dictionaries from 1895 were consulted as well as a book entitled 'Glue and Gelatin' from 1923. As stated by the Portuguese Dictionary, the term *glue* (''*colla''*) refers to 'a glutinous material that has the intention of holding, joining and attaching paper, wood, etc (pp 112)' [39]. The French Dictionary mentions that *glue* manufacture (''*colle*'') 'comprises cooking to gelatinous solution' and has different purposes, such as to photography, ceramics, porcelain and glass (pg.348)' [40]. Both dictionaries do not include the term *gelatine*. Lastly, the 'Glue and Gelatin' book gives more detailed information concerning these terms. As for *glue* it is stated that it is an 'organic colloidal substance of varying appearance, chemical composition and physical properties, obtained upon drying the solution resulting from boiling with water properly prepared animal matter such as skin and bone' (pp 11). The term *gelatine* is 'made from bone and skin or hide fragments, selected, cleaned and treated with especial care so that the resulting product is clearer, purer and generally cleaner and light in colour than glue' (pp 11-12). However, to complicate matters in terms of clear definitions, Alexander also states that glue is an impure gelatine, and any glue possessing suitable strength and appearance may be termed gelatine [41].

In this dissertation, the term *size* is referred to the glutinous solution used to spread over the canvas during the preparation of the fabric for painting as described above and *gelatine* is assigned to the material that was obtained by hydrolysis of the collagen present on the ligaments, cartilages and tendons of the animal, which therefore was used as *size*.

Witlox, in her PhD thesis on historical paint preparation layers (1550-1900), found documentary evidence that glues used to size painters' supports were made usually from animal skins as well as

[12] http://www.merriam-webster.com/dictionary/gelatin,accessed 22-06-2015.
[13] http://www.merriam-webster.com/dictionary/glue, accessed 22-06-2015.

parchment and glove clippings. Between 1800-1849, 22 recipes of a total of 58 called for animal glue, while 6 mention the use of a flour paste size and 30 do not mention the size layer at all. Even between 1850-1899, only 10 recipes of a total of 24 mention the use of animal glue, whereas 1 indicates a flour paste size and 12 do not mention sizing for canvas preparation (pp 137-138) [16].

What is interesting about the layer on the portrait, is that due to its extreme thickness (3x the size layer found in reconstructions (mentioned previously), and its ability to span the large space between the threads in the mesh canvas, it does not appear to conform to the size layers made with preparations from animal hides or glove leather (see Fig.VII.1, Appendix VII.1). It is significant that ''gelatine'' is being called for in Vibert's recipes which are close to the time the portrait was painted, which, for the purposes of this research is being interpreted as a common term for the time which refers to a commercial product introduced in the 19th century.

5.4.1 Reconstructions of size layers - Experimental details

Vibert's recipes (Appendix VIII.1, VIII.2) specifically calls for '*gelatine*' and given the knowledge about the range of additives that are likely present in modern industrial gelatine, as mentioned above, it was necessary to obtain a minimally modified gelatine to represent what would have been used in the nineteenth century. The raw material chosen for the reconstructions should be able to give a strong and cohesive film since the visual appearance of the size layer suggests these characteristics. Vibert states that ''*gelatine*'' can be obtained from either animals skins or bones (1892, pg.103) [5]. To get more knowledge of what animal source should be used, other historical recipes were consulted[14] and the animal mentioned the most was the calf, although other sources (e.g. sturgeon, sheep, goat, rabbit and cow) might be used. For the purposes of reconstructing a fine and pure adhesive the calf (most specifically the hooves) was chosen. It is also important to note that the age of the animal is important since it will influence the dissolution of the collagen. Collagen from older animals is reported to be more cross-linked, and more difficult to dissolve [27].

Since industrial methods for obtaining gelatine could vary (the study of which is beyond the scope of this thesis), and would be at a different scale than the needed for the laboratory reconstructions, a domestic source for producing gelatine was chosen. During the Victorian era (1837-1901), a writer emerged and published a famous cookery book: Isabella Beeton (né Mayson, 1836-1865)[15]. She wrote extensively on cooking and household management for her husband's publications (Samuel Beeton). By 1861, her famous ''*The Book of Household Management*'' became available and described recipes as well as childcare, etiquette and household management. This mid-nineteenth century standard source for cookery provides a recipe for gelatine extraction using the hooves of calves (pages 596-597). The recipe was scaled-up in order to obtain sufficient gelatine for the reconstructions (Appendix VIII.5).

Six calves' feet (total weight 7,75 kilos) previously sliced in half by the butcher, were placed into a large stainless steel cooking pots and gradually brought to boil using *Serra da Estrela* spring water (Appendix VIII.6). The recipe mentions boiling times of 6 to 7hours, but only 3 hours was needed to

[14] Carlyle database on 18th & 19th century oil painting materials, available through Leslie Carlyle
[15] http://www.bbc.co.uk/history/historic_figures/beeton_mrs.shtml, accessed 25-07-2015.

boil the calves hooves fully[16]. It was left over night in a refrigerator (approximately 4ºC) to cool and set. On the following day all the fat was removed from the top and the jelly was wiped with a cleaned cotton cloth and the sediment on the bottom of the jelly was removed. The jelly was then filtered twice, first through cotton gauze and then using coffee filters, since with the first option the filtering was not very successful as some small particles of undissolved matter and bone were still visible within the gelatine solution. The resulting liquid was of a light yellow colour.

The final gelatine obtained was in a jelly state (Fig.10) and could be easily re-dissolved at 40ºC using a bain Marie. When it reached liquid state it was applied on two canvases[17] and thick Melinex® (100 microns) sheets (see Appendix IX.3) with a flat hogshair brush #8 (bristles size 2cm long by 1.5cm wide) and with a stainless steel spatula on two pilot supports made in rigid card (foam-core)[18] (Appendix IX.3). For the final application to the canvases for the project, a system was used of layering the gelatine first vertically, then horizontally and again vertically to guarantee that the holes between the threads were all covered with the gelatine, as well as on the surface of the Melinex® sheet. Canvas was chosen for the application of the reconstructions in order to attempt a possible replica by achieving the same visual properties as the size layer on the portrait. Melinex® was also used as a second substrate, to provide pure films and for ease of producing samples for study without any canvas fibres. With the combination of visual appearance and the analytical results the major aim was to identify what can be established as a reference material. The size layers were applied in the laboratory at room temperature (20ºC) with a low relative humidity (33%). The low RH accelerated the drying time and also to minimise glue degradation since under high humidity levels glue undergoes microbiological attack, therefore causing degradation [27].

Figure 10 – Final gelatine obtained.

5.4.2 Reconstructions - Vibert's recipes

Vibert's recipes for treating gelatine for use in preparation layers for oil paintings are not very straightforward, since there are details missing. Vibert mentions very often using ''*a little*'' of a material, which is not useful as a measure. For that reason it was necessary to repeat the recipes with different proportions of materials to establish what ''*a little*'' might mean in the context of the recipe results. The use of stepped proportions of ingredients has the added advantage of providing quantitative information for calibrating instrumental analyses. Stepped proportions help to confirm if the analytical tools used during analysis can determine the relative amount of extenders used (e.g. alum, aluminum acetate, or glycerine). It is important to establish the detection limits since they can be below what is called for in recipes, and can help establish the lowest limits of a substance detectable [43].

[16] This might be related to the use of a modern electric heat source, since it is not the same as used in the 19th century.
[17] The two canvases are open weaved linen canvas. Before using the canvases were washed in tap water, then stretched, dried and re-stretched. Before application a scheme was drawn using masking tape to map all the future samples, which would involve different layer thickness and proportions (Appendix IX.3).
[18] The construction of foam cards with fabric involved cutting squares (5cm by 5cm) and posteriorly attaching the open weaved linen with magic tape to the foam card (see Figure IX.1).

Table IX.1 (Appendix IX.1) summarises the recipes chosen from Vibert and the reconstructions which were made.

Each sample was applied to two substrates: a wide mesh canvas and a sheet of Melinex® (100 microns, see Appendix IX.3) and each received a unique code, so that all samples could be easily recognized and counted. A spreadsheet (Appendix IX.2) was also done to show the proportion of the ingredients used. During preparation, care was taken to prevent contamination, and to take appropriate safety measures when dealing with hazardous materials.

One of the main aims of this project was to ascertain the effect of the various additions to the gelatine called for in Vibert's recipes and to discover which would or would not relate to the treatment of the size on the portrait.

Besides Vibert's recipes, reconstructions were also made from a recipe by W.H. Davies, from the field of photography. His recipe was reproduced on page 140, in *The Painted Photograph (1839-1914): origins, techniques, aspirations*, published in 1996 (Appendix VIII.4) [51]. The recipe dates from 1870 and includes both gelatine and gum lac for application on canvas (for photographs on canvas). Davies provides more specific information than Vibert. Given the fact that µ-FTIR suggested the possibility of having gum lac within the size layer on the portrait, it was of utmost importance to do reconstructions from Davies's recipe.

5.5. Results - Observation during preparation and application

To determine the weight of gelatine needed to fill five test squares on the canvas (each square was 5cm x 5cm). V.PG-1 was used which consisted of the gelatine alone (see Appendix IX.1 for an explanation of the sample codes used). A beaker was filled with cold V.PG-1 to the 30ml mark[19] then was weighed. A layer of gelatine was applied by passing the brush over the canvas vertically, then horizontally then vertically again for a total of 3 times in each of five squares. This application took approximately 4mls of pure gelatine. It was possible to conclude that 4mls covered an area of 50cm^2. During application of the differently prepared gelatines, it was felt that recipes which produced a gel were more economical than liquid, since less quantity is used on each layer applied due to the presence of a full layer underneath. This was also noted by some authors [15,16,17]. Liquid glue gets absorbed by the threads and does not easily form a layer. Prior to spreading, all samples were warmed (~40ºC) in a Bain Marie.

By mixing alum with gelatine (V.GAl) it was noticed that as it cooled the solution stayed liquid longer than the gelatine alone (V.PG-1). This allowed a longer working time, although it was not less viscous than V.PG-1 (gelatine). No real change in behaviour was noticed according the amount of alum added until the proportion with 1g alum (V.GAl-6), since it coagulates. With the addition of both starches (rice and potato –GRis and GPos) the gelatine was more granular. The same was noticed with the sample GTRf (gelatine, turpentine and rice flour). The addition of shellac increased the viscosity of the gelatine as more shellac was added (D.GS-5; D.GS-4; D.GS-3; D.GS-2; D.GS-1 and D.GS-1.5; D.GS-1.4; D.GS-1.3; D.GS-1.2 and D.GS-1.1).

The majority of samples were spread with the gelatine in the form of a gel, except for the V.G1 series (V.G1v, V.G1a, V.GRs, V.G1.SCG, V.G1.MCG), which consisted of the gelatine with glacial

[19] 30mls mark corresponds to 22g. After melting in bain Marie the volume was approximately 22mls.

acetic acid, and vinegar that remained very liquid. In all of these reconstructions the liquid was absorbed by the threads, consequently there was no layer formation. D.GS-1 and D.GS-1.1, consisting of gelatine and bleached shellac were also unsuccessful in forming a film since the proportion of 1g gelatine to 9g shellac was too liquid to form a layer. Strong deformations (bulges) in the open weave canvas were observed with sample GAl-6 (consisting of 5g gelatine to 1g alum). It also coagulated partially and did not stay fluid very long (it appeared to be very sensitive to temperature since it coagulates as it cooled). Apart from GAl-6, the other samples with alum did not show evidence of planar distortion. There is a clear difference on the surface of GAl-6 and the other alum containing formulation because it created a distinctly white layer and the canvas is much more rigid. Most of reconstructions painted out onto the canvas have a shiny surface, except V.GBs-1, V.GBs-3 (gelatine and bleached shellac) and GRis-1, GPos-1 (gelatine with rice and potato starches, respectively), and V.GTRf-1 (consisting of gelatine, turpentine and rice flour) (see Table IX.2).

Regarding the application on thick Melinex® (Fig.IX.2), each sample was applied in one layer and all samples were similar in behaviour and appearance to pure gelatine with no obvious extra fluidity in application. However, the sample with 1g alum (V.GAl-6) coagulated and dried quickly during application. Samples containing both bleached and red shellac (V.GBs-1;-2 and GRs-1) could not be applied as both formed a sticky material that became stuck within the bristles of the brush.

Attempts to make the solution gelatine, bleached shellac and borax (V.GBx) were frustrated since the solution did not dissolve properly and the final resulted obtained was always a gum like material with improperly dissolved particles of borax ($Na_2B_4O_7.10H_2O$). This is related to the fact that this reconstruction was dissolved in water and not in alcohol like the previously mentioned samples with bleached and red shellac (V.GBs and V.GRs set).

5.5.1 .Results- Observation of dried reconstructions

After the samples were completely dry, a visual evaluation was carried out in order to establish which reconstructions should be studied further, with the aim of possibly providing reference materials to help identify the method used to render the size in the portrait unresponsive to moisture, and to evaluate the effect of the ingredients called for in Vibert's recipes. Images of these layers are provided below. Most of the samples kept their appearance in terms of colour (they were colourless), except the set with chrome compounds (V-GBP), since the chrome renders an orange/yellow tonality. This colour change is mentioned by Vibert (p.189). Six months after application and exposure to room light, the set of chrome samples (V-GBP) with the highest amounts of chrome lost colour intensity and the size film was no longer visible (just an overall dark orange colour that is impregnated into the threads), the exception were samples which contained the lowest amounts: V.GBP-5 (20g gelatine and 0.13g bichromate of potash) and V.GBP-6 (20g gelatine to 0.07g bichromate of potash). Both formed a uniform layer, due to the lower amounts of chrome present in each sample.

Regarding the gelatine and glycerine samples (V.Ga set), as Vibert predicted, the addition of glycerine did render the gelatine supple[20] with increasing amounts (by drops) of the glycerine. Overall these samples form an even layer. It is interesting to note that reconstructions made with aluminium acetate (Table IX.2) did not form a layer, but when the aluminium source was changed to alum (sulphate aluminium potassium dodecahydrate, Al K $(SO_4)_2.12H_2O$), all concentrations of alum with gelatine formed a coherent layer. The gelatine containing shellac from Davies's recipe (D.GS-5 and D.GS-1.5) had the closest visual appearance and morphology (solid and uniform layer) to the size on the portrait. A higher proportion of gelatine proved to be important to achieve an even layer between the threads, but in the case of the shellac, only the proportions of 9g gelatine and 1g shellac (D.GS-5 and D.GS-1.5), had the strength needed to produce a solid layer. In fact, Vibert states that shellac gives strength to the gelatine, although no proportions are mentioned in his recipe. The other proportions of gelatine and shellac (D.GS-1,2,3,4 and D.GS-1.1;.2;.3;.4) (Table IX.2) did not form a uniform film on the canvas and therefore, are not acceptable as a size layer. Reconstructions containing rice (GRis) and potato (GPos) starch form layers but have minor holes within the layer between the threads and the size is opaque not translucent like the other samples. Lastly, the recipe with gelatine, turpentine and rice flour (GTRf) formed a cohesive layer with a beige colour but unlike the other reconstructions its surface is matt, not shiny (Fig.11).

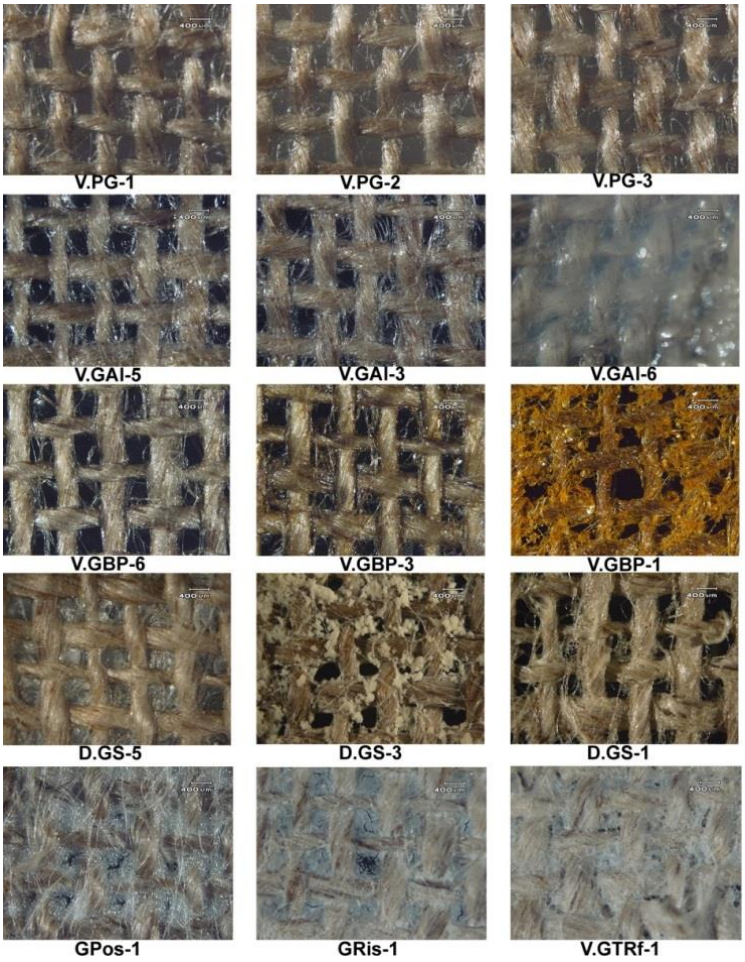

Figure 11 – Macro images of different size layer reconstructions.

5.6. RH and water sensitivity tests- Results

The RH and water sensitivity tests described above were also carried out for samples from the reconstructions. Samples were selected from reconstructions considered viable as a size layer, since not all of the recipes were successful in forming a film (see Table X.1, Appendix X.2). The set with the addition of alum remained water and RH sensitive, especially in relation to the amount of alum present, the lower the amount, the greater the RH sensitivity. Regarding the water tests, all samples from the alum set (V.GAl) dissolved fully. From the set containing bichromate of potash (V.BGP),

[20] This was noticed during sampling preparation.

those with the three last proportions (V.GBP-4; V.GBP-5 and V.GBP-6) did not suffer a significant change relative to RH tests and did not dissolve in the water tests. The reconstructions confirm what Vibert states, that by adding the bichromate of potash, the gelatine is unresponsive to moisture and insoluble in water [5]. Samples from reconstructions from Davies's recipe which include shellac (D.GS-5 and D.GS-1.5), exhibited very low dimensional change and did not dissolve in the RH and water tests respectively. Regarding the reconstructions with rice and potato starch (GRis-1, GPos-1) and V.GTRf (gelatine, turpentine and rice flour) all remained RH sensitive and water sensitive.

5.7. Analysis of the reconstructions

Samples from selected reconstructions were analysed with the following: µ-FTIR, SEM-EDX and Py-GC/MS (see Appendix X.3).

The gelatine alone (V.PG) was characterized by the spectral fingerprints of a typical protein based material (with the Amide A, I, II and III bands) [28].

To ascertain the detection limits of µ-FTIR, samples from gelatine reconstructions with the greatest and least amount of added material were chosen for analysis.

In sample V.GAl-5, containing the lowest amount of alum (0.0007g alum; 5g gelatine - 0.01 wt/wt %), the typical SO_4^{2-} anion from the alum structure was not detected. Only the presence of a protein based material, with the same spectral fingerprints as gelatine alone. In the sample containing the highest proportion of alum (V.GAl-6), with 1g and 5g gelatine (16.7 wt/wt %), µ-FTIR did detect the SO_4^{2-} anion along with the protein.

When the alum source was changed, it was possible to distinguish between the alum containing compounds with µ-FTIR. Sample V.GAA-5, containing the lowest amount of aluminium acetate (0.0007g and 5g gelatine – 0.01 wt/wt %) indicated the CO_2^{4-} ion from its structure.

Reconstructions containing the most (0.12g glycerine and 5g gelatine - 2.3 wt/wt %) and least (0.03g glycerine and 5g gelatine – 0.6 wt/wt %) amount of glycerine (V.Ga-4 and V.Ga-1, respectively), both indicated the presence of the glycerine and the protein.

Analyses were also carried on samples containing shellac. In sample D.GS-1(consisting of 1g gelatine to 9g shellac) the spectra essentially indicates the profile of the shellac. However, in sample D.GS-5 (9g gelatine to 1g shellac), the same shoulder (Amide I band) was found as in the portrait's size (Figure 12). In relation to the original size (**A**), the same characteristics (referred previously) were confirmed with this proportion (**B**), although it indicates a loss of C-H bonds, which might suggest that the sample is heterogeneous.

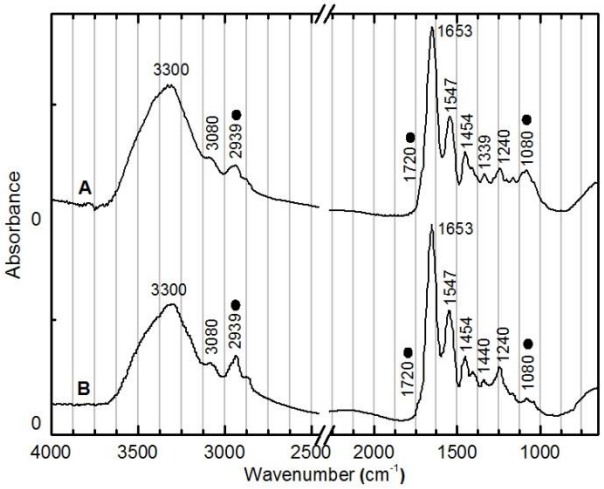

Figure 12 - µ-FTIR spectrum of portrait's size layer (**A**) and D.GS-5 sample (**B**).

SEM-EDX analysis allowed the identification and location of Aluminium (Al) in V.GAl-5 and Chromium (Cr) in V.GBP-6 (see Table X.2, Appendix X.3). What is also very interesting to notice, is the presence on both analysis of reconstructions the

presence of the Sodium (Na) and Chlorine (Cl), which might suggest the presence of sodium chloride (NaCl), the same salt encountered in the portrait's size sample (S4). SEM also permitted the characterisation of the morphology of the different reconstructions, with different types of material within the collagen source visible in the backscattered images (see Figure 13). Rounded aggregates of granules with different particle sizes were visible in the sample containing 12,26g gelatine to 2g rice starch (G.Ris) (Fig.13A). In the sample containing 9g gelatine to 1g shellac (D.GS-5), the collagen exhibits micelle-like areas (Fig. 13B). This could be related to the emulsion formed when the gelatine and shellac are mixed together (observed during the preparation of this sample). Lastly, the collagen morphology appears unaltered in samples containing alum (0.0007g) (Fig.13C), chrome (0.07g) and glycerine (0.12g) (V.GAl-5, V.BGP-6 and V.Ga-4, respectively), compared to the pure gelatine.

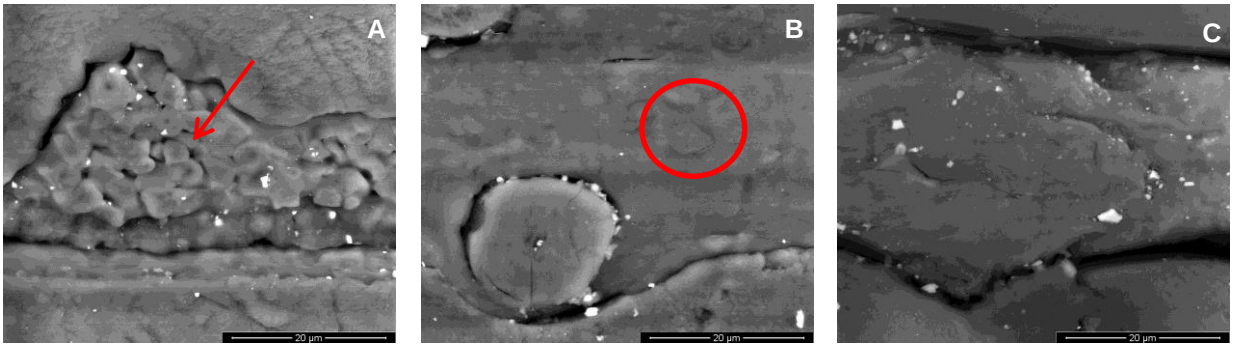

Figure 13 – SEM images. A is reconstruction G.Ris, showing rounded aggregates; B is reconstruction D.GS-5 indicating the micelle-like areas and C is reconstruction V.GAl-5 where the collagen appears to be unaltered.

Since a reconstruction with shellac (D.GS-5- 9g gelatine to 1g shellac) showed a similar spectral fingerprint in µ-FTIR, as the size from the portrait, it was particularly important to verify if the ''shoulder'' could be related to the presence of shellac. A complementary analytical technique which provides detailed compositional information is Py-GC/MS. This technique has the capability of separating and identifying characteristic hydroxyl aliphatic and terpene acids associated with shellac [50]. Reference samples of both shellac and gelatine (which had been used in the reconstructions) were analysed. The full set of different proportions of shellac and gelatine (set D.GS) was then analysed to establish whether all stepped proportions of shellac were detected and quantifiable. The analysis carried indicated that of all the different proportions in this set (D.GS) it was possible to detect both the gelatine and shellac products (see Table X.2, Appendix X.3).

As for the analysis of the portrait's size, pyrolysis did not show evidence of shellac, but did indicate the presence of 3.7% of products not characteristic of reference samples of gelatine. Three of these products remain unidentified with amounts of 1.5%, 1.3% and 0.5% respectively. The fourth product, representing 0.4%, was identified as 3,4-dimethoxy-benzoic acid and methyl ester (most probably methylated vanillic-acid, which is an oxidized form of vanillin). Vanillin has a spectral fingerprint that exhibits absorption bands near 1700cm^{-1}, near the same bands found in the portrait's size (that displayed by the ''shoulder''). Although possibly associated with gelatine as a flavouring agent, to date, no specific reference for its use in gelatine recipes has been found. However, Beeton notes (See Appendix VIII.5) that commercial gelatine could have an unpleasant taste, which suggest flavouring agents may well be added [52].

6. CONCLUSIONS

In Part 1, the detailed research regarding the study of the medals and the background history of the sitter was carried out to place the sitter in context, and to evaluate whether there were any alterations (additions) to the sitter's uniform. No additions and alterations were found.

Tracing the prepared canvas and stretcher to a French source within a specific date range (due to the stencil mark present on the back of the painting) led to a better understanding of the materials present in the painting and their larger context (as French prepared, ''*toile ordinaire*'') as well as establishing the earliest date that the canvas could have been prepared. With this information it was possible to justify the use of Vibert's recipes for gelatine sizes since his book was published with the period that these canvases were available commercially. The fact that Vibert was producing commercial products based on his published recipes adds validity to reconstructing his recipes.

Regarding the treatment, this work revealed the importance of anticipating each step. For example, during surface cleaning, the first colours to be cleaned were the whites, in order to establish the true colour of the dirt, so that this could be compared with the colour of the swab from other areas of the painting. Another example of anticipating each step is related to the alignment of the canvas threads in the tear area. This was carried out prior to flattening the distortions in the canvas associated with the tear. If the area was flattened first, then the threads would not be aligned along the tear. Another example of anticipating future steps was related to the need to take all relevant micro samples (in this case from both the size layer and ground) prior to treatment, since the sampling area was later covered with fill and samples were no longer available.

Surface cleaning, restricted to dust and dirt removal only, resulted in a profound change in the appearance of the image, due to the high proportion of dust and dirt present. Varnish removal, while considered, was not felt to be necessary as it was anticipated that the change in the appearance of the image would not be as significant.

The greatest challenge during the treatment was to choose appropriate infill materials, to overcome difficulties with the very thin layers of infill required while achieving a shallow textured infill that could match the surface of the original paint exactly. The latter was a demanding task that required patience and practice. Nevertheless the final result was gratifying.

In Part 2, the reconstructions project provided important information, firstly the history of commercial gelatine which was essential to determine the significant changes in animal sources and manufacturing processes over time. Reconstructions with historically appropriate materials and using recipes contemporary to the period of the painting, provided information on the behaviour of a range of additives to the gelatine during and immediately after application, and then as reference samples for analytical techniques, to establish detection limits, and for comparison with the portrait's size layer.

The RH and water sensitivity tests, developed for this thesis proved a low-cost, efficient method for evaluating the behaviour of the size on the portrait and the reconstructions.

A particular challenge was the interpretation of Vibert's recipes, since he rarely provided specific amounts of ingredients. This was overcome by making variations using a range of different compounds (e.g. alum, aluminium acetate or bichromate of potash compounds) and making reconstructions with additives in stepped proportions. These reconstructions are highly characterised

and provide useful reference materials which can be available for future research beyond this specific project. Over time, the more aged the samples will get, the better, since the chemical interaction can be studied (particularly in the bichromate of potash, since changes in colour (fading) have been evident already.

Reconstructions of gelatine size with stepped proportions of added compounds were particularly important for a better understanding of the detection limits of the analytical instruments used. The use of complementary instruments was also important since they can provide different information which all together can help with the interpretation of the data.

The size layer reconstructions which showed the most similarity in appearance and behaviour to the portrait's size were made with the gelatine and shellac (D.GS set) since it was unresponsive to RH and water tests like the portrait's size and appeared most similar in the μ-FTIR spectra. Nevertheless, Py-GC/MS of the D.GS set could detect shellac while in the original size was disappointing since no shellac resin was detected. As a consequence, analytical results based on the reconstructions made, were not able to establish the method used to render the portrait's size layer unresponsive to moisture and water.

Another relevant finding was the presence of compounds related to methylated vanillic-acid, a flavouring agent, which was present in the portrait's size layer. This might point to the use of a commercial gelatine intended for domestic use, which establishes a closer relationship to Vibert's recipes for treating what appears to be commercial gelatine sizes for use in oil painting preparation layers.

The use of a widely available commercial product intended for domestic use (and presumably for photography as well) in a size layer is an interesting innovation in the field of paintings materials, and until now, has not been studied.

The lack of moisture (RH) and water response of the size layer plays a significant role in the current state of the painting, which is remarkably in plane and taught on its original stretcher. The behaviour of this painting to changes in ambient RH, compared with another more traditional oil painting of similar dimensions[21] in the paintings laboratory at the same time, which showed dramatic planar distortions in high RH, demonstrates the effectiveness of the materials used in the portrait. It is likely that the use of a mesh canvas with very thin threads plays an important role in the stability of this painting to RH fluctuations. As suggested by painting materials researcher, Jilleen Nadolny[22], the ratio of cellulosic material within the whole painting composite, is much reduced in comparison with a more traditional canvas, which will also reduce RH response since the canvas is particularly responsive to fluctuations.

Unfortunately, the long-term stability of this painting is questionable given the SEM evidence of delamination at the ground-size interface. This painting will require monitoring to establish whether flaking of the paint/ground composite will become a problem in the future.

[21] Oil painting dated 1951. Artist: Henrique Medina; Title: Portrait of Manual Carlos de Freitas Alzina, Visconde de Merceana. Dimensions (cm): length 68 x width 55.
[22] Personal communication with Dr Jilleen Nadolny, February, 2015.

Future Research

For future research the role of the sodium chloride in the size layer and the delamination problem between the ground and size would be an important area of focus. As well, a greater understanding of the complex varnish layers present would be useful in terms of their interpretation regarding the technique of varnishing with retouch varnish and a final varnish. More research to identify the green particles used in the figure's sash is needed, since the current results are inconclusive.

For the painting as a whole, an interesting area for future work would be the materials and techniques used in ''painted photographs'' [51], which were popular at the time of this painting. Photographic images were made on what appears to be a normal canvas support then covered with oil paint to give the appearance of an original oil painting. Since gelatine was used as a carrier for photographic images, the adoption of a commercial gelatine for the size layer in the portrait may have a connection to its use in photography, or even in relation to painted photographs.

A more detailed study of the gelatine animal source would be interesting to ascertain if different trace elements could be detected relating to the animal's food source.

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APPENDICES

A digital Appendix (DVD-R) is supplied with this thesis in order to provide high resolution images of the treatment of *Januário Correia de Almeida*.

APPENDIX I – BEFORE TREATMENT PHOTOGRAPHS OF *JANUÁRIO CORREIA DE ALMEIDA*

Figure I.1 – Normal Light, front.

Figure I.2 – Normal Light, back.

Figure I.3 – Raking Light from the right side.

Figure I.4 – Ultraviolet (UV) Light.

Figure I.5 – Infrared (IR) Light.

Figure I.6 – *Januário* x-radiograph.

APPENDIX II – BEFORE TREATMENT DETAILS OF *JANUÁRIO CORREIA DE ALMEIDA*

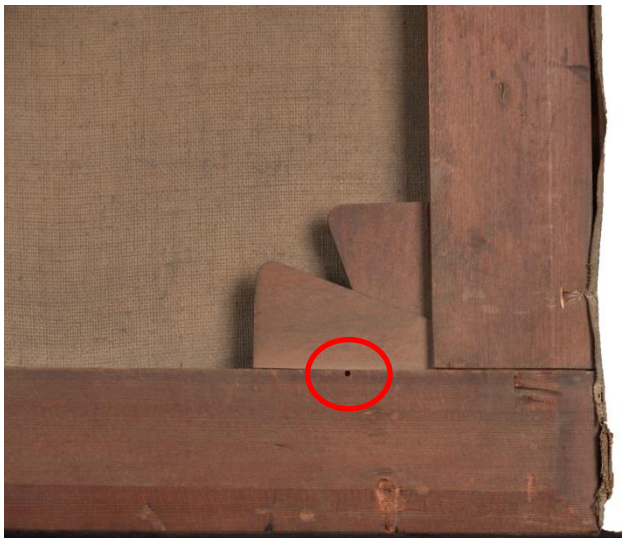


Figure II.1 – Back of the canvas indicating presence of exit hole.

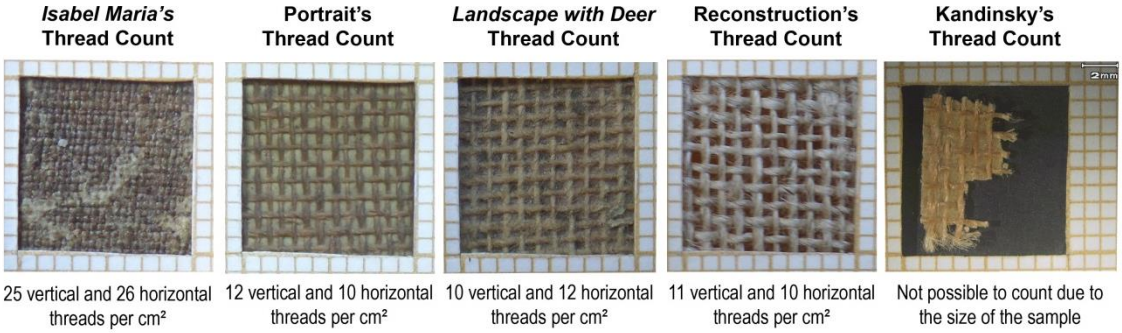


Figure II.2 – Baxter Method applied on different types of fabric to compare thread count.

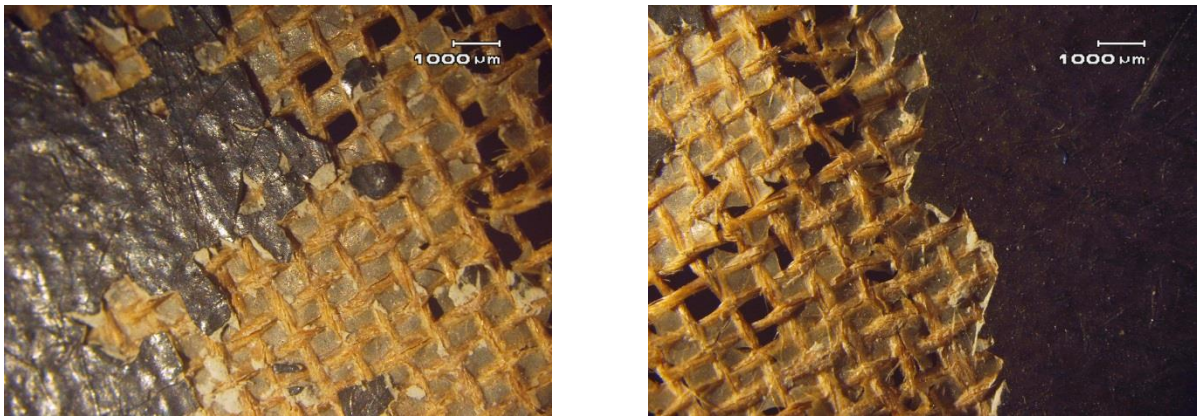
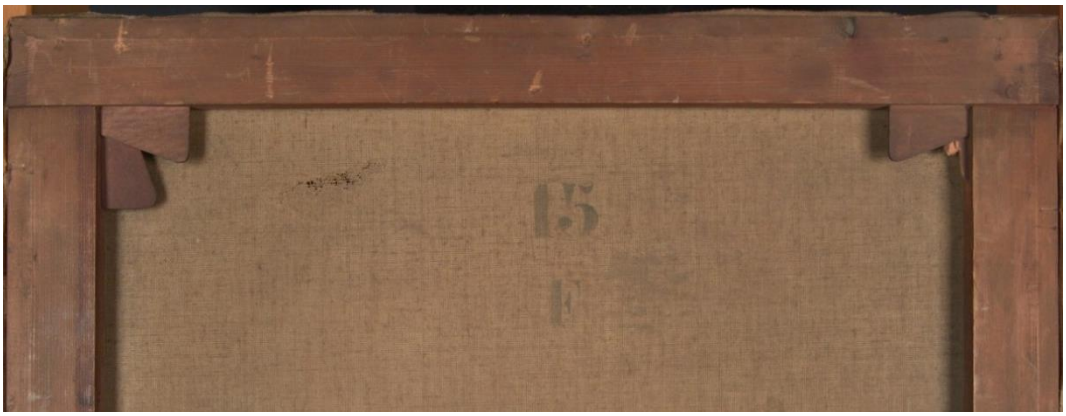


Figure II.3 – Detail of missing paint composite associated with the tear. The size layer is visible between canvas threads.



TOILES POUR PEINTURE A L'HUILE TENDUES SUR CHASSIS

NUMÉROS	DIMENSIONS FIGURE	DIMENSIONS PAYSAGE	DIMENSIONS MARINE	TOILE ORDINAIRE CHASSIS ordinaires carrés	TOILE ORDINAIRE CHASSIS à clés, carrés modèle déposé (1)	TOILE ORDINAIRE CHASSIS ordinaires ovales	TOILE 1/2 FINE CHASSIS à clés, carrés modèle déposé (1)	TOILE FINE CHASSIS à clés, carrés modèle déposé (1)	TOILE FINE CHASSIS à clés, ovales anciens
	m. m.	m. m.	m. m.	fr. c.	fr. c.	fr. c.	fr. c.	fr. c.	fr. c.
1	0 22 × 0 16	0 22 × 0 14	0 22 × 0 12	» 60	» 65	1 50	» 70	» 85	3 50
2	0 24 × 0 19	0 24 × 0 16	0 24 × 0 14	» 65	» 75	1 60	» 80	1 »	3 75
3	0 27 × 0 22	0 27 × 0 19	0 27 × 0 16	» 70	» 85	1 75	» 95	1 20	4 »
4	0 33 × 0 24	0 33 × 0 22	0 33 × 0 19	» 80	1 05	2 »	1 20	1 50	4 75
5	0 35 × 0 27	0 35 × 0 24	0 35 × 0 22	» 90	1 25	2 25	1 40	1 75	5 50
6	0 41 × 0 33	0 41 × 0 27	0 41 × 0 24	1 »	1 50	2 50	1 70	2 20	6 »
8	0 46 × 0 38	0 46 × 0 33	0 46 × 0 27	1 30	1 75	3 »	2 10	2 70	6 50
10	0 55 × 0 46	0 55 × 0 38	0 55 × 0 33	1 50	2 25	3 75	2 70	3 55	8 50
12	0 60 × 0 50	0 60 × 0 46	0 60 × 0 38	1 80	2 55	4 25	3 10	4 15	9 50
15	0 65 × 0 54	0 65 × 0 50	0 65 × 0 46	2 »	3 »	4 50	3 60	4 85	11 »
20	0 73 × 0 60	0 73 × 0 54	0 73 × 0 50	2 50	3 50	5 75	4 20	5 70	12 50
25	0 81 × 0 65	0 81 × 0 60	0 81 × 0 54	2 80	4 15	6 75	5 05	6 80	14 »
30	0 92 × 0 73	0 92 × 0 65	0 92 × 0 60	3 30	5 15	7 50	6 30	8 55	15 »
40	1 » × 0 81	1 » × 0 73	1 » × 0 65	4 25	6 10	9 »	7 55	10 15	20 »
50	1 16 × 0 89	1 16 × 0 81	1 16 × 0 73	5 25	7 65	11 »	9 35	12 75	22 »
60	1 30 × 0 97	1 30 × 0 89	1 30 × 0 81	6 25	8 95	13 »	11 05	15 15	28 »
80	1 46 × 1 14	1 46 × 0 97	1 46 × 0 89	8 20	11 60	16 »	14 30	19 70	32 »
100	1 62 × 1 30	1 62 × 1 14	1 62 × 0 97	10 »	14 65	20 »	18 05	24 80	36 »
120	1 95 × 1 30	1 95 × 1 30	1 95 × 1 14	12 »	18 15	22 »	22 20	30 30	40 »

(1) Voir figure, page ci-contre.

NOTA. — Les Châssis *hors mesure* sont livrés dans les 24 heures de la réception de la Commande.

Figure II.4 - Back of the canvas showing stencil mark ''F'' and ''15'' and table of standard stretchers from *Bourgeois aîné*, published in a catalogue from 1888 (reproduced from p.46 [11]).

Figure II.5 – Detail of small paint/ground losses.

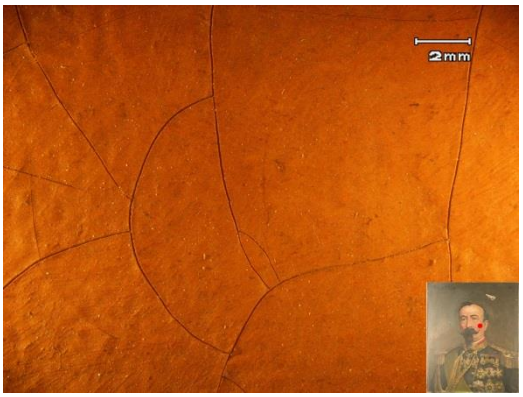
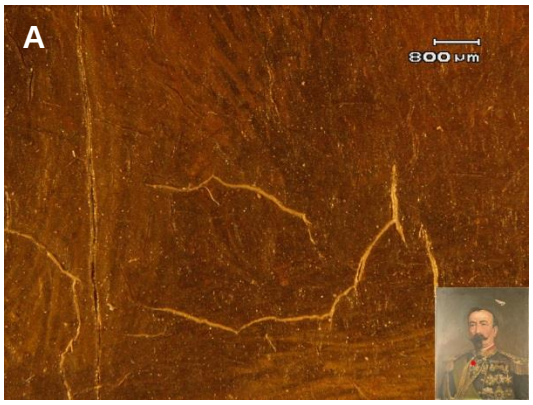


Figure II.6 – Detail of mechanical crack.



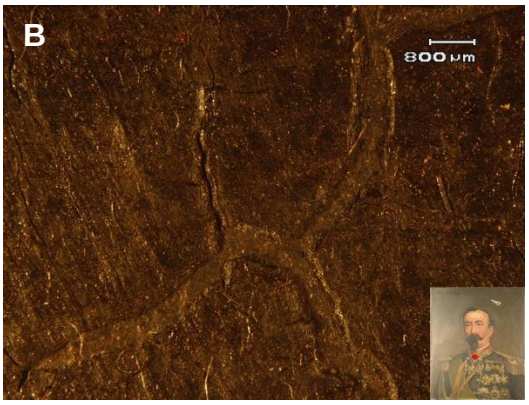


Figure II.7 A and B – Details of drying cracks.

Figure II.8 – Detail of opaque dark coating.

Figure II.9 – Detail of different fluorescence'.

Figure II.10 – Detail of paint application.

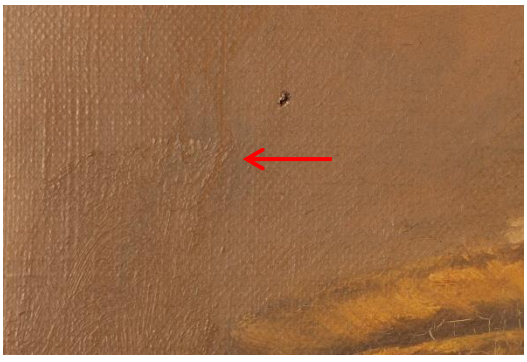


Figure II.11 – Detail of drips and different shades.

APPENDIX III – *JANUÁRIO CORREIA DE ALMEIDA'S* CHRONOLOGY AND AWARDS

Portugal is proud to have a long tradition in the assignment of rewards by the Head of State for services rendered to the country, these take the form of decorations [6]. Januário earned a total of 17 decorations and 3 titles. A summarized table is shown below with all the information regarding the medals that was possible to identify in the painting.

Figure III.1 – Identification of medals present in the oil painting [6].

Table III.1 – Name of Military Orders/Medal identified.

Number	Name of Military Order/Medal
1	Portuguese Military Order of Villa Viçosa (Breast Badge)
2	Portuguese Gold Medal for Good Services (Breast Badge)
3	Portuguese Gold Medal for Exemplary Conduct (Breast Badge)
4	French Legion D'Honneur (Breast Badge)
5	Portuguese Military Order of Tower and Sword, Value, Loyalty and Merit (Grand Cross Star)
6	Portuguese Military Order of Avis (Grand Cross Star + Green Sash)
7	Brazilian Military Order of the Rose (Breast Bagde)
8	Portuguese Military Order of the Christ (Breast Badge)
9	Portuguese Military Order of Villa Viçosa (Grand Cross Star)
10	Spanish Military Order of Isabella the Catholic (Grand Cross Star)
11	Portuguese Military Order of Tower and Sword, Value, Loyalty and Merit (Grand Necklace)

On the 9th of February, 1870 King D.Luís nominated Januário as Governor General of India with the task of reorganizing the administration as well as minting new currency. Within a year the Governor organized the postal services to implement new postal regulations, replacing that previously implemented by Portuguese in India in 1865 [3].

In 1874, Januário was appointed minister plenipotentiary in China, Japan and Siam, and got China to recognize the rights of Portugal in the Peninsula of Hai Nan, as well as organizing the consular service in Japan. When he returned to Lisbon in 1875 he became one of the founders of the Geography Society of which he was the honorary president.

APPENDIX **IV** – MAP OF DAMAGES

Figure IV.1 – Mapping of the painting condition.

APPENDIX V – MATERIAL ANALYSIS

Appendix V.1- Instrument Description

Most of the analytical instruments used are from FCT-DCR, with the exception of: the SEM-EDX which belongs to the Portuguese microscopy network REM, at CEMUP- Centro de Materiais, Universidade do Porto and the Py-GC/MS owned by Instituto Superior de Agronomia- Universidade de Lisboa.

❖ **Photographic Documentation**

Studio photographs were acquired using a Sony Digital Camera (DSC-F828, Cyber-shot, Zeiss, Super HAD CCD, 4colour. 7x optical zoom. 8.0Mega-pixels). For photographs under UV light, the camera was equipped with a UV filter (Hoya Pro1Digital Filter. Tokina Co., Ltd. DCM, 58) and for Infrared light (IR) photographs an IR filter (Hoya, 58mm Infrared R72) was used. During treatment details, were taken with a Nikon COOLPIX S3100 and a Samsung WB800F.

❖ **X-radiograph**

The X-radiograph was obtained using an ArtXRay from NTB electronische Geraete GmbH digital system. This system is composed of a X-ray generator Y.MBS/160-F01, with a directional beam with a focal spot size of 1,9mm, a 40-160kV voltage, 0,2-5,0mA current and a maximum X-ray power of 480W; a manipulator of 4µm/step and 5000streps/revolution resolution; and a camera with a 10-160kV radiation sensitive range, 0,083mm pixel size, and 12pixel/mm resolution.

For the X-radiograph the following conditions were used: 60kV and 2,4mA with 100ms of integration time. The digital images were acquired and processed with iX-Pect software.

❖ **Optical Microscopy (OM)**

The optical microscope is an Axioplan 2ie Zeiss microscope equipped with a transmitted and incident halogen light illuminator (tungsten light source, HAL 100); UV light (mercury light source, HBO 100 illuminator); and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for microphotographs. Samples were analysed with 10x ocular lenses and 5x/10x/20x/50x objective Epiplan lenses (giving total optical magnification of 50x, 100x, 200x and 500x).

For the incident and transmitted light (normal light) the samples were analysed under crossed polars- polarizer and analyser filters; and for UV light the Zeiss filter set 2 [BP 300-400, FT 395, LP 420] was used. The scales for all objectives were calibrated within Nikon ACT-1 software.

❖ **Stereomicroscope**

Detail photographs were taken with an Olympus SZX12. Stereomicroscope with a 7x to 90x zoom range, equipped with an integrated Olympus DP12 digital camera and a Schott KL 200 external cold light source with two flexible optic fibre cables.

❖ **Energy Dispersive X-Ray Fluorescence (µ-EDXRF)**

X-rayfluorescence spectra were achieved using an ArTAX spectrometer from Intax GmbH. Operating with a molybdenum (Mo) X-ray tube, focusing polycapillary lens and silicon drift electro-thermaly cooled detector and a xFlash (Si drift) detector, with 170 eV resolution. The accurate positioning system and polycapillary optics enable a small area of primary radiation (ø~70µm) at the sample. Elemental compositions were obtained from the average three independent spots, analysed with a tube voltage of 40KV and a current intensity of 600µA and live time 100s.

❖ **µ-Raman**

Micro-Raman microscopy was accomplished using a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 17 mW power operating at 632.8 nm and an external laser of 50mW power operating at 532 nm. Spectra were recorded as an extended scan. The laser beam was focused with a 506 Olympus objective lens (50x). The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities 0.3, 0.6, 1). The spectra are shown as acquired, without corrections or any further manipulations.

❖ **Fourier Transform Infrared Spectroscopy (μ-FTIR)**

Infrared spectra were obtained using a Nicolet Nexus spectrophotometer coupled to a Continumm microscope (15x objective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, between 4000-650 cm^{-1}, resolution setting 4 cm^{-1} and 128 scans, using a Thermo diamond anvil compression cell. The spectra are shown as acquired, without corrections or any further manipulations, except for the removal of the CO_2 absorption at ca. 2300-2400 cm^{-1}.

❖ **Electron Scanning Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX)**

SEM images were obtained using a FEI Quanta 400 FEG ESEM, with a Schottky emitter field emission gun, operating at low vacuum conditions and at 15 kV, equipped with an EDAX Genesis X4M detector. Images were acquired using secondary (SE) and backscattered (BSE) electron detectors.

❖ **Pyrolysis- gas chromatography-mass spectrometry (Py-GC/MS)**

Py-GC/MS analysis were performed with an automated microfurnace pyrolyzer Frontier Lab PY-3030S with an Auto-Shot Sampler (AS-1020E) attached to an Agilent GC 6890 with mass selective detector MSD 5973N. Pyrolysis runs were performed at 600 ºC for 10 sec, pyrolysis products were separated in a DB 1701 (60 m × 0.25 mm, 0.25 μm film, J&W Scientific) column. All samples were derivatized with 3μL of 5% TMAH in methanol.

Appendix V.2 – Sampling areas for Cross-Sections (S), μ-FTIR (F), μ-EDXRF points and Py-GC/MS (P)

Figure V.1 – Sample areas for Cross-Sections (S), μ-FTIR (F), μ-EDXRF points (·) and Py-GC/MS (P).

Table V.1 – Code for identification of cross-sections (left) and µ-FTIR and Py-GC/MS sample (right).

Sample	Colour / Area
S4	Size layer (area of tear)
S5	Ground and size layers (tacking margins)
S6	Dark green (sash)
S7	Dark green (sash)
S8	Background (right side of the figure)
S9	Background (near area of tear)
S10	Dark green (sash)
S11	Black tone (black uniform)
S12	Dark green (sash)

Sample	Area
µ-FTIR	
F1	Size layer
F2	Ground
F3	Green sash
Py-GC/MS	**Area**
P1	Size layer

Appendix V.3 – Cross-Sections. Normal light (left) and Ultraviolet light (right)

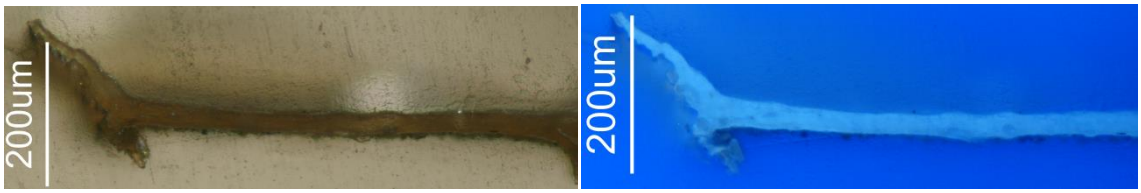


Figure V.2 – Cross-section S4, showing the thickness of the size layer on the portrait.

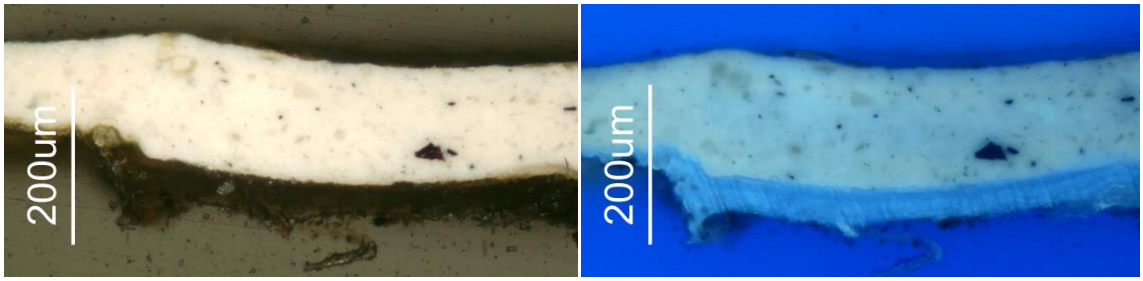


Figure V.3 - Cross-section S5, showing both the ground and size layers on the portrait.

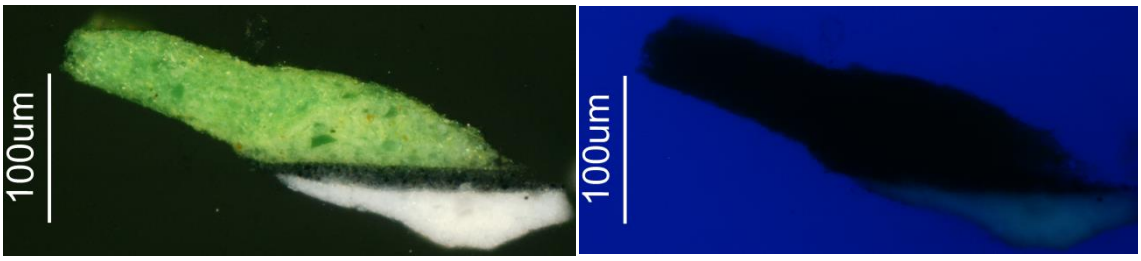


Figure V.4 - Cross-section S6, showing ground and paint layers from the sash on the portrait.

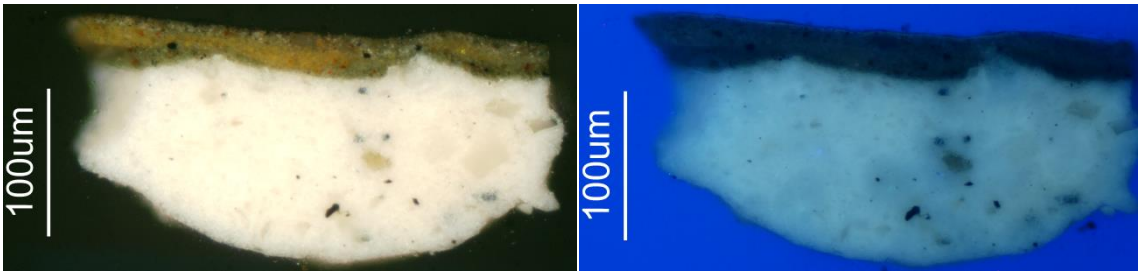


Figure V.5 - Cross-section S8, showing ground and paint layers from the background.

Appendix V.4 – Fibre Identification

By using OM it was possible to identify the fibres present on the canvas as bast fibres, likely flax. Usually throughout the 18th and 19th century the main fabric supports used were linen and hemp [14].

By observing the longitudinal view of the fibre (Fig.V.6), cross marks (x-shaped joint-like as well as transverse cross marks) along the fibre and rainbow interference colours are visible. These are characteristics of bast fibres [14]. Due to the similarity of both flax and hemp fibres in longitudinal orientation, it is difficult to differentiate them. Therefore, in order to distinguish between linen and hemp fibres, a cross-section was made (Fig.V.7), where it was possible to affirm by transverse view, flax fibres, since these fibres display the narrow polygon shape of the boundary as well as the rounded outline and the oval lumen at its center, characteristic of flax (linen). Reference images[23] are displayed to indicate the differences (Fig.V.8, V.9).

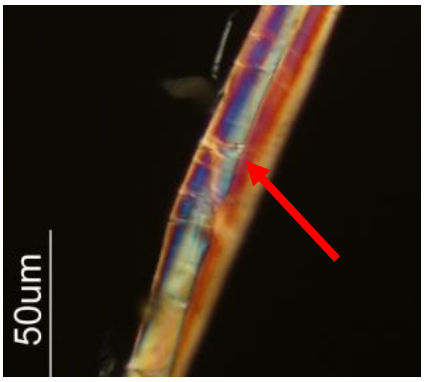


Figure V.6 – Longitudinal view of a fibre from the canvas under OM: cross polarised light, total magnification 50x. Red arrow indicates cross-marking (x-shaped).

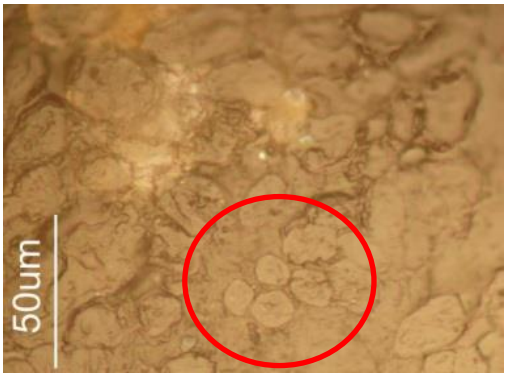


Figure V.7 – Transverse view of a fibre from the canvas. Red circle indicates rounded shape with central lumen.

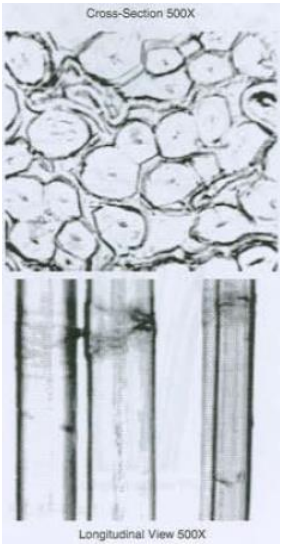


Figure V.8 – Reference images of flax. Transverse view (top) and longitudinal view (bottom) of fibre.

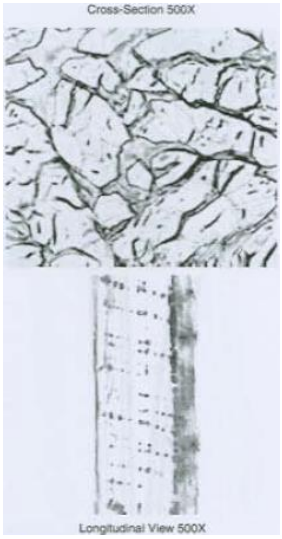


Figure V.9 - Reference images of hemp. Transverse view (top) and longitudinal view (bottom) of fibre.

[23] Reference images described by AATCC Teste Method 20, *Fiber Analysis: Qualitative* (2004, page 44).

Appendix V.5 – Materials Identification Table

Table V.2 – Materials analysis from the ground (visible as white material in normal and UV light).

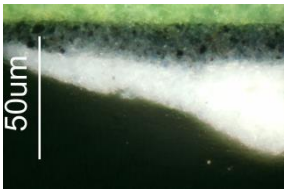
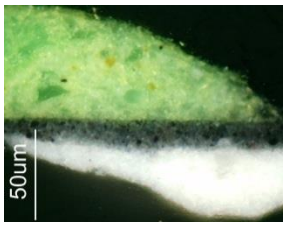
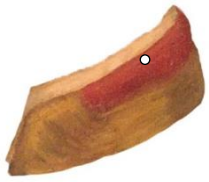
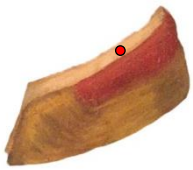
Portrait cross-sections'								
	Sample	μ-EDXRF	SEM-EDX	μ-Raman		μ-FTIR		Materials Identified
				Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	
Ground	  Normal and UV light image from Cross-Section S6 ground layer (white), paint layers (green) are analysed in Table V.3.	(Ca), (Ba), **Fe**, **Cu**, **Zn**, (Hg), **Pb**	**Pb**	1047vs-1050vs	$\nu_s(CO_3^{2-})$	1407s 682m	$\nu_{as}(CO_3^{2-})$ $\delta_{in\text{-}plane}(CO_3^{2-})$	Lead White $2PbCO_3.Pb(OH)_2$
			Ba	453m-460m 986vs-988vs	- $\nu_s(SO_4^{2-})$	1180m; 1118s; 1076vs 983w	$\nu_{as}(SO_4^{2-})$ $\nu_s(SO_4^{2-})$	Barium Sulphate $BaSO_4$
			S, Ca	-	-	-	-	Calcium Sulphate Dehydrate $CaSO_4.2H_2O$ (?)
			P, Ca	-	-	-	-	Calcium Phosphate $CaPO_4$ (?)
			F, Ca	-	-	-	-	Fluorite CaF_2 (?)
			S, Zn	-	-	-	-	Zinc Sulphide ZnS (?)

Table V.3 – Pigments identified in the Portrait's paint layers and ground layers.

Portrait cross-sections'								
	Sample	μ-EDXRF	μ-Raman		μ-FTIR		Pigments Identified	
			Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment		
S6 - Green Sash		(Ca), (Ba), **Cr**, **Fe**, **Cu**, **Zn**, (Hg), **Pb**	-	-	**1590vs** **1410s**	$\nu_{as}(COO^-)$ $\nu_s(COO^-)$	Copper Carboxylate [47]	Paint Layers
			360s; 380m 842vs	$\delta(CrO_4^{2-})$ $\nu_s(CrO_4^{2-})$	**1097m 1047w** **880w 855w** **833w**	$\nu_{as}(SO_4^{2-})$ $\nu_{as}(CrO_4^{2-})$	Chrome Yellow $PbCrO_4$	
			250vs; 283w 342m	δ (S-Hg-S) ν (Hg-S)	-		Vermilion HgS	
			546vs 810w	$\nu_s(S_3^-)$ -	-		Ultramarine Blue (possibly the synthetic form) $Na_8[Al_6Si_6O_{24}]S_n$	
			1340vs (br) 1600vs (br)	sp^3 (C-C) sp^2 (C-C)	-		Carbon Black	
			See Table V.2					Ground Layers
S8 –Background		(Ca), (Ba), **Fe**, (Cu), **Zn**, (Hg), **Pb**	-	-	-		-	Paint Layers
			See Table V.2					Ground Layers

Yellow Sample from Medal	 Medal from where sample was taken	(Ca), **Cr**, (Fe), Cu, **Zn**, (Hg), **Pb**	336m; 357s; 376m; 398m 838vs	δ (CrO_4^{2-}) v_s(CrO_4^{2-})	-	Chrome Yellow $PbCrO_4$	
Blue Sample from Medal	 Medal from where sample was taken	(Ca), (Cr), Fe, **Cu**, **Zn**, (Hg), **Pb**	256w 547vs 810w 1096m	δ(S_3^-) v_s(S_3^-) - overtone	-	Ultramarine Blue (possibly the synthetic form) $Na_8[Al_6Si_6O_{24}]S_n$	
Red Sample from Red Collar	 Collar from where sample was taken	(Ca), (Ba), **Fe**, **Hg**, **Pb**	252vs; 283w 342m	δ (S-Hg-S) v (Hg-S)	-	Vermilion HgS	
White Sample from White Collar	 Collar from where sample was taken	(Ca), (Ba), **Fe**, **Pb**	1048vs	v_s(CO_3^{2-})	-	Lead White $2PbCO_3.Pb(OH)_2$	

Appendix V.6 – µ-FTIR spectra analysis

❖ Ground analysis

By performing µ-FTIR analysis on a sample of the ground from the edges of the tacking margins, it was possible to confirm the materials present since there are characteristic bands of lead white ($2PbCO_3.Pb(OH)_2$) at 1407 and 682cm^{-1} as well as barium sulphate at 1180, 1118, 1076 and 983 cm^{-1} (see Table V.2 for assignments). The aged oil binder displays characteristic bands at 2927 and 2854 cm^{-1} (CH_2 asymmetric and symmetric stretching modes, respectively); at 1732cm^{-1} (C=O stretching mode from the ester bond and carboxylic acid) and at 1540cm^{-1} which resembles metal carboxylates [46,47]. According to Carlyle, p.516, barium sulphate was commonly used as an additive to lead white paint in the 19th century [15].

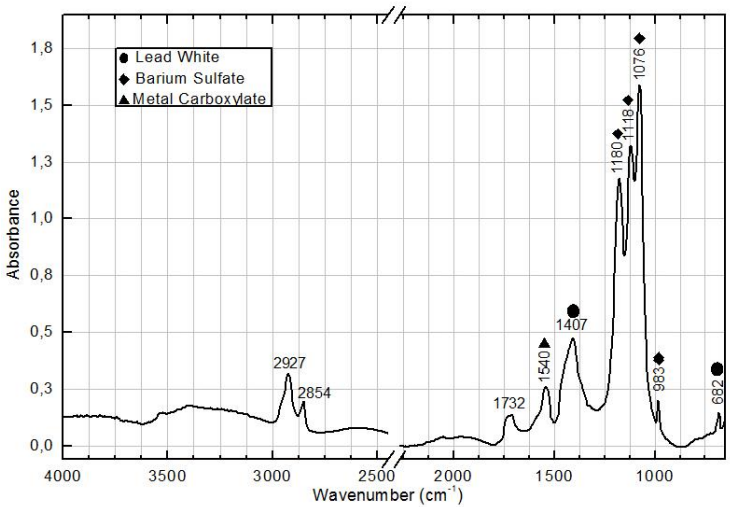


Figure V.10 - µ-FTIR spectrum of a ground sample.

APPENDIX VI –TREATMENT PHOTOGRAPHS

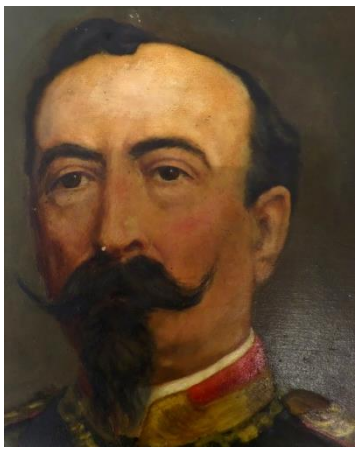


Figure VI.1 – Detail of face during surface cleaning showing the top half cleaned.

Figure VI.2 – Local moisture treatment with moist blotter forming a bridge over the tear. Before tear repair.

Figure VI.3 – Thread realignment using raking light and 10x magnification optivisors.

Figure VI.4 – Detail of tear repair during treatment, right side has been repaired, left side has not.

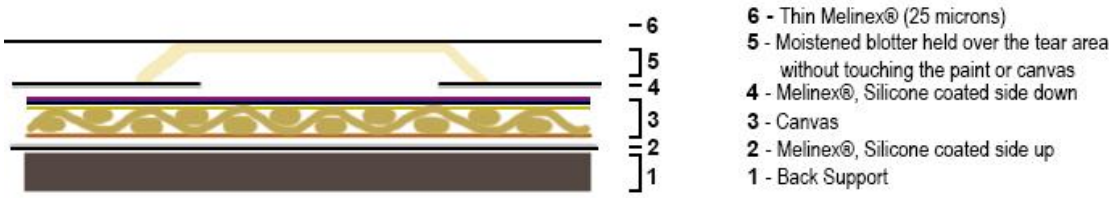


Figure VI.5 – Diagram of the system used during flattening.

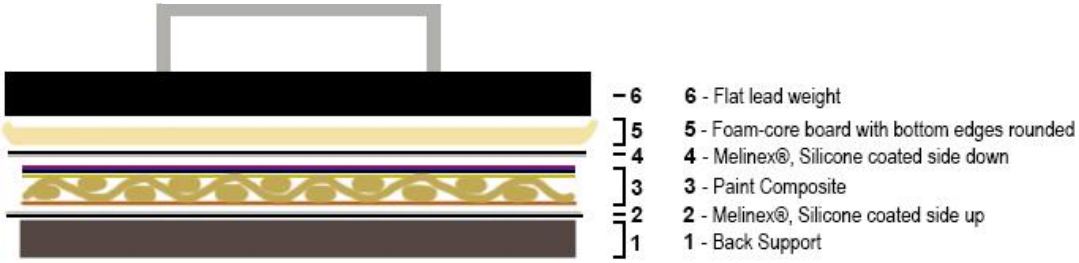


Figure VI.6 – Diagram showing the system used to achieve a plain surface.

Figure VI.7 – Flattening of tear area with light weights on top of silicone coated Melinex®.

Figure VI.8 – Detail image of BEVA®371 and kaolin.

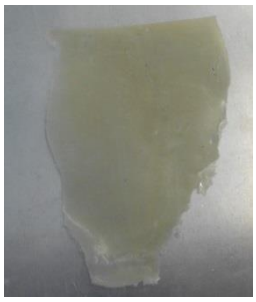


Figure VI.9 – Appearance of BEVA®371 and kaolin after being heated between sheets of thin silicone coated Melinex®.

Figure VI.10 – First layers of the infill material.

Figure VI.11 – Cork covered with polyester fabric used to smooth surface of the infill.

Figure VI.12 – Appearance of textured fill before softened.

APPENDIX VII – SIZE LAYER STUDIES

Appendix VII.1- Size layers: comparison of cross-sections. Normal light (left) UV light (right)

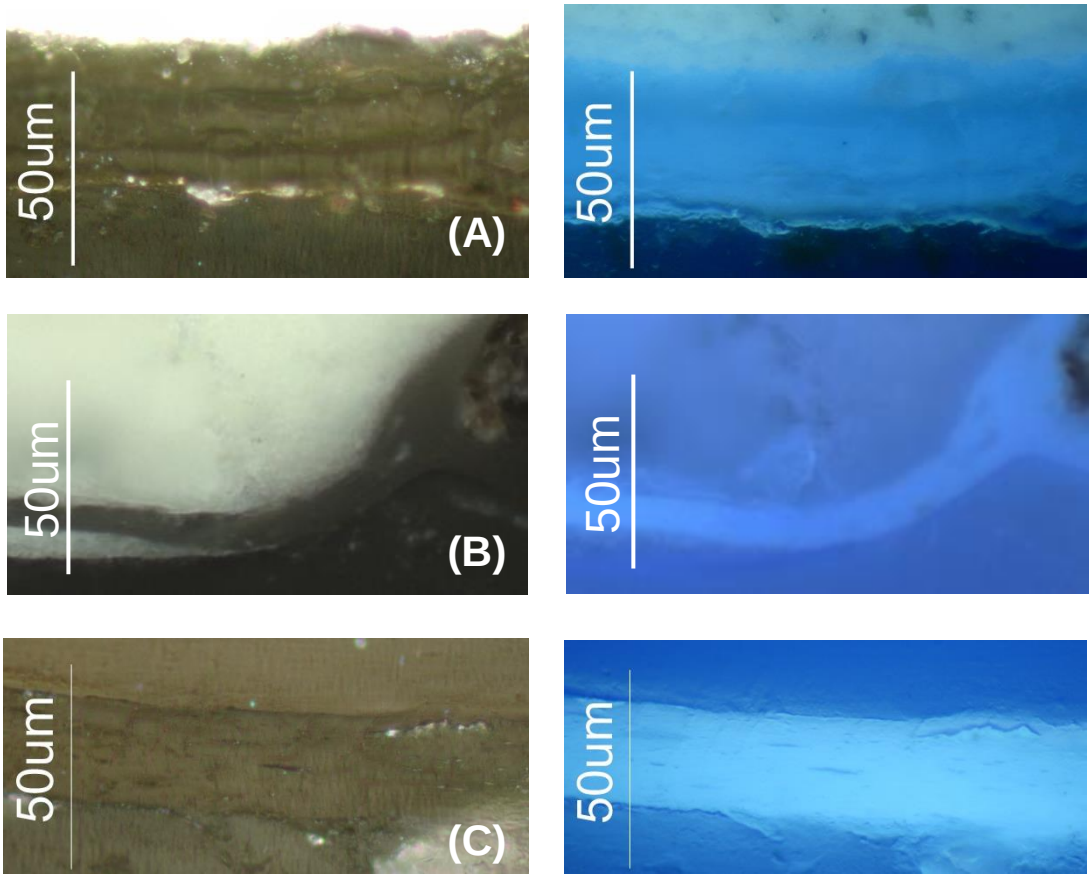


Figure VII.1 – Cross-sections of (A) portrait's size showing layer thickness; (B) HART sample EX10, size layer- under a layer of chalk and glue showing thickness and (C) size from *Landscape with Deer* painting, showing layer thickness.

Appendix VII.2- RH and water sensitivity tests

Table VII.1- RH and Water Sensitivity Testing.

Sensitivity Tests						
Sample	**RH Test, 3 days at 99% RH**			**Water Test, cold water immersion**		
	Measurement before	Measurement after	Difference	Measurement before	Measurement after	Difference
Portrait	**Overall:** 0.45mm x 0.221mm; **thickness:** 0.0025mm	**Overall:** 0.41mm x 0.214mm; **thickness:** 0.0026mm	**Overall:** 0.012mm^2; **thickness:** 0.0001mm	**Overall:** 0.589mm x 0.425mm; **thickness:** 0.021mm	**Overall:** 0.554mm x 0.343mm; **thickness:** 0.025mm	**Overall:** 0.06mm^2; **thickness:** 0.004mm
7% RSG	**Overall:** 0.782mm x 0.457mm; **thickness:** 0.082mm	**Overall:** 0.664mm x 0.429mm; **thickness:** 0.104mm	**Overall:** 0.937mm^2; **thickness:** 0.022mm	Dissolved		
Kandinsky	**Overall:** 0.744mm x 0.460mm; **thickness:** 0.196mm	**Overall:** 0.836mm x 0.573mm; **thickness:** 0.216mm	**Overall:** 0.112mm^2; **thickness:** 0.02mm	**Overall:** 0.300mm x 0.398mm; **thickness:** 0.162mm	**Overall:** 0.316mm x 0.400mm; **thickness:** 0.175mm	**Overall:** 0.006mm^2; **thickness:** 0.013mm
Landscape with Deer	**Overall:** 0.480mm x 0.453mm; **thickness:** 0.020mm	**Overall:** 0.473mm x 0.484mm; **thickness:** 0.040mm	**Overall:** 0.002mm^2; **thickness:** 0.02mm	Dissolved		

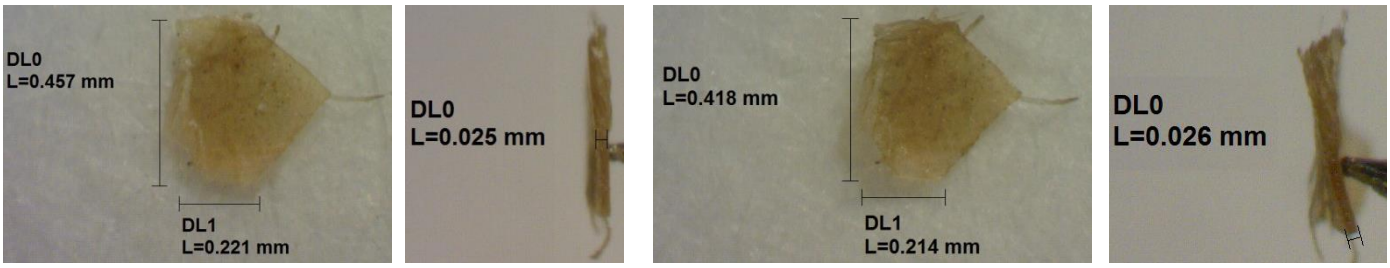


Figure VII.2 – Portrait's size: RH tests, measurements before (left) and after (right).

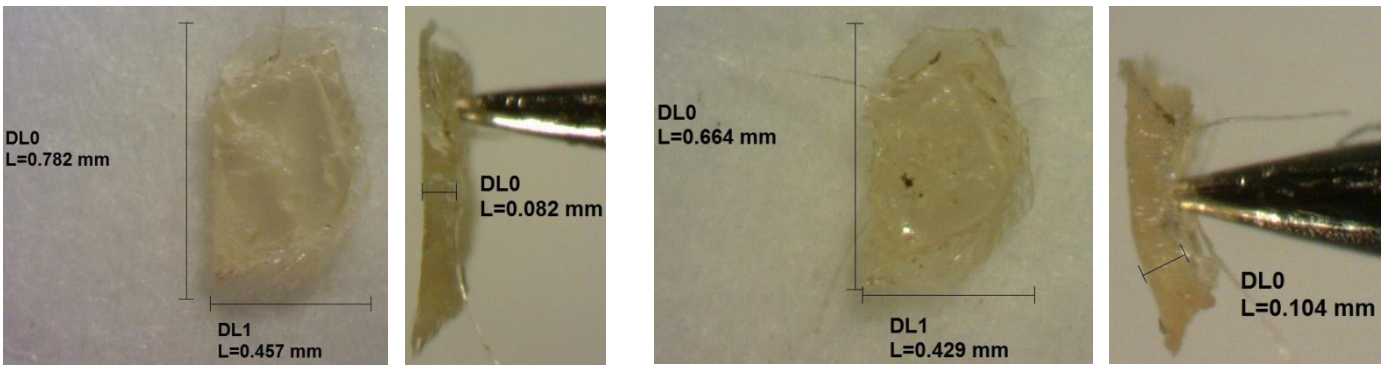


Figure VII.3 – 7% RSG: RH tests, measurements before (left) and after (right).

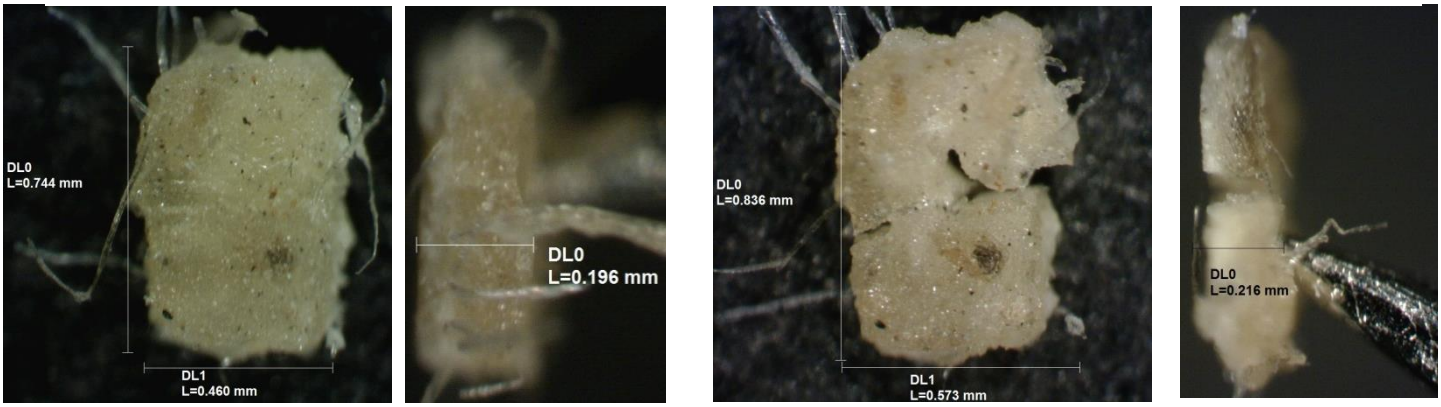


Figure VII.4 – Kandinsky's size: RH tests, measurements before (left) and after (right).

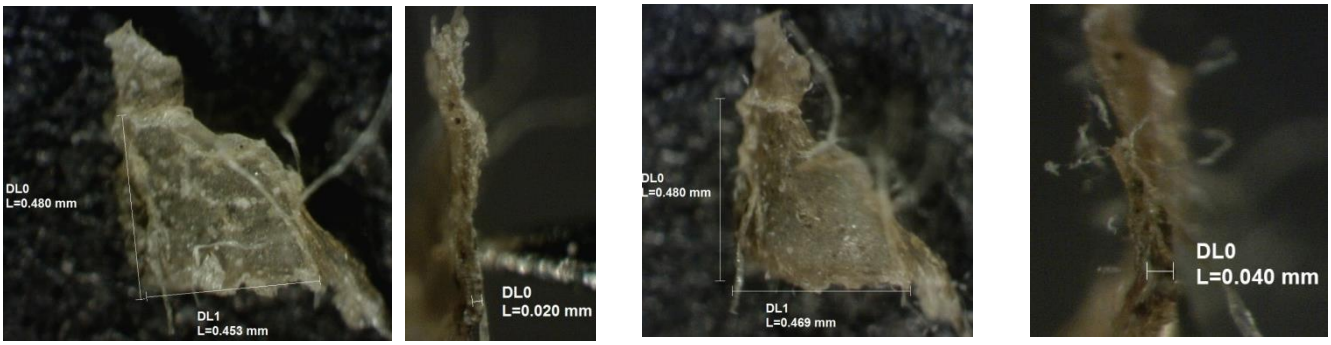
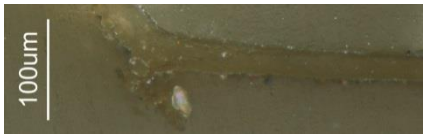


Figure VII.5 - *Landscape with Deer's* size: RH tests, measurements before (left) and after (right).

Appendix VII.3- Analysis of size layers

Table VII.2 – Analysis of two different size layers.

Cross- sections' from two different size layers						
Sample		**SEM-EDX**	**μ-FTIR**		**Py-GC/MS**	**Material Identified**
			Wavenumber (cm^{-1})	Assignment	Products Found	
S4- Portrait's size		**C, Ca,** K, S, Pb	3300 (br); 3080m; **2939m**; **1720w**; 1653vs; 1547s; 1454s; 1340m; 1250s; **1080m**	N-H stretching; 2x C-H stretching; 2x C=O stretching; C-N-H bending; C-H bending and 2x C-O stretching	Pyrolysis products of gelatine (same as V.PG- see Table X.2) and presence of vanillin	Protein based material, that displayed a ''shoulder''. Bands marked in bold suggest presence of vanillin (?)
		Na, Cl	-	-	-	Sodium Chloride NaCl (?)
Landscape with Deer size		**C, Pb, Ca, Na, Al**, S, Zn	3300 (br); 3080m; 1653vs; 1547s; 1454s; 1340m; 1250s	N-H stretching; C-H stretching; C=O stretching; C-N-H bending; C-H bending and 2x C-O stretching	-	Protein based material

APPENDIX **VIII** – RECIPES

Appendix VIII.1- Jehan George Vibert. *The Science of Painting*. 1892. pg.189

'Gelatine.
To render gelatine liquid (*i.e.* to prevent it from becoming a jelly when cooling), dissolve the white gelatine in its weight of the following liquid:-

Half acetic acid and half water ¾
Alcohol at 95 degrees ¼
Add a little alum.

To render the gelatine supple, a little glycerine is added, in different quantity according to the degree of suppleness desired.

To add strength to the gelatine, some gum lac may be added to it, either in alcoholic solution, or in solution with water and borax.

Gelatine mixed with linseed oil and our picture varnish makes an emulsion which, ground with zinc white or white lead, makes sizings drying slowly but of wonderful solidity; when they are to be painted over we do not advise their use, preferring the sizing of casein paste to them, but in certain cases they may be useful. To render the gelatine insoluble, it should be added to a mixture composed of one part chromic acid to five parts of gelatine or of bichromate of potash and left to dry in plenty of light; but in this condition the gelatine is of a yellow colour.

If it be desired to preserve the gelatine uncoloured and liquid whilst rendering it insoluble, we prefer the following means:

Gelatine	1
Water	10
Acetic Acid	3
Acetate of aluminium	3

Add a little alcohol when all is melted. On all occasions when gelatine contains acetic acid, care must be given not to mix it with colours which are carbonates.'

Appendix VIII.2- Jehan George Vibert. *The Science of Painting*. 1892. pg.190

‘The starch or farina should be put into cold water, and thoroughly mixed; when the starch or farina no longer forms lumps, put it on the fire, keep stirring, and take it off after it reaches boiling point. Starch paste with gelatine and turpentine (resin) makes a very good paste, that dries quickly.

Boil (together) in water

Starch	100gr.
Gelatine	50 ’’
Turpentine	50 ’’ ’

Appendix VIII.3- General information about Jehan George Vibert

According to Carlyle, in *The Artist’s Assistant*, 2001: ‘’Jehan George Vibert wrote *Le science de la peinture* which was translated as *The Science of Painting* (by Percy Young) and published in London in 1892. This is a very important work for its comments on the methods and materials in use throughout the century. Vibert belongs with a group of authors publishing in the last twenty year of the nineteenth century who were attempt to apply scientific principles to solve problems concerning the durability of contemporary painting materials (pg.11)’’ [15].

Appendix VIII.4- W.H. Davies, ‘’European Method of Printing on Canvas’’, *Anthony’s Photographic Bulletin*, February, 1870, p.2, as cited in *The Painted Photograph (1839-1914), page 140* [51]

‘’Take from four to six grains of gelatine, soak it an ounce of water for an hour, then melt it gently over a fire, hot plate, or water-bath, using a clean earthern pipkin. When fully dissolved, add to it, while yet warm, and stirring it gently during the mixturing, from four to six drachms of a solution of white lac in methylated spirit, if for white, or pale surfaces; but orange lac will do if the surface be of a darker colour. This is made in the proportion of six ounces of spirit to one ounce of lac, and digesting it till fully dissolved. The mixture of the gelatine and gum lac in spirits produces a creamy-looking emulsion, to which is added four grains of chloride of sodium, or a like equivalent of chlorides of ammonium or barium, and, when fully dissolved, filter through fine muslin into a clean pipkin, and it is ready for use.’

Appendix VIII.5- S.O. Beeton, *The Book of Household Management*, 1859-1861, p. 596 [52]

‘To make the stock for jelly, and to clarify it.
1411. Ingredients: 2 calf’s feet, 6 pints of water.
Mode: The stock for jellies should always be made the day before it is required for use, as the liquor has time to cool, and the fat can be so much more easily and effectually removed when thoroughly set. Procure from the butcher's 2 nice calf's feet: scald them, to take off the hair; slit them in two, remove the fat from between the claws, and wash the feet well in warm water; put them into a stewpan, with the above proportion of cold water, bring it gradually to boil, and remove every particle of scum as it rises. When it is well skimmed, boil it very gently for 6 or 7 hours, or until the liquor is reduced rather more than half; then strain it through a sieve into a basin, and put it in a cool place to set. As the liquor is strained, measure it, to ascertain the proportion for the jelly, allowing something for the sediment and fat at the top. To clarify it, carefully remove all the fat from the top, pour over a little warm water, to wash away any that may remain, and wipe the jelly with a clean cloth;
remove the jelly from the sediment, put it into a saucepan, and, supposing the quantity to be a quart, add to it 6 oz. of loaf sugar, the shells and well-whisked whites of 5 eggs, and stir these ingredients together cold; set the saucepan on the fire, but ***do not stir the jelly after it begins to warm***. Let it boil about 10 minutes after it rises to a head, then throw in a teacupful of cold water; let it boil 5 minutes longer, then take the saucepan off, cover it closely, and let it remain 1/2 hour near the fire. Dip the jelly-bag into hot water, wring it out quite dry, and fasten it on to a stand or the back of a chair, which must be placed near the fire, to prevent the jelly from setting before it has run through the bag. Place a basin underneath to receive the jelly; then pour it into the bag, and should it not be clear the first time, run it through the bag again.

This stock is the foundation of all *really good* jellies, which may be varied in innumerable ways, by colouring and flavouring with liqueurs, and by moulding it with fresh and preserved fruits. To insure the jelly being firm when turned out, 1/2 oz. of isinglass clarified might be added to the above proportion of stock. Substitutes for calf's feet are now frequently used in making jellies, which lessen the expense and trouble in preparing this favourite dish; isinglass and gelatine being two of the principal materials employed; but, although they may *look* as nicely as jellies made from good stock, they are never so delicate, having very often an unpleasant flavour, somewhat resembling glue, particularly when made with gelatine.

Time: About 6 hours to boil the feet for the stock; to clarify it,--1/4 hour to boil, 1/2 hour to stand in the saucepan covered.'

Appendix VIII.6- Observations during extraction of gelatine

The recipe was carried out step by step as described. Half of one calf's weighted 690.6 grams (although not all weighted exactly the same since some were larger than others, the total weight of calf's feet used was 7,75 kilos). A total of 11 liters of *Serra da Estrela* spring water were used and distributed in three stainless steel pots. The FCT-PNT pot (the biggest) had the capacity of having six half's (corresponding to three feet) and the small pots had three half's in each. The small pots had 2 liters of water and the largest had approximately 4.40 liters. The heat was turned on at 10:30 on 4 February 2015. The scum described in the recipe appeared 1st at 10:50 and was continuously removed using a stainless steel sieve until 11:47. It was noticed that the scum at the beginning was of a brownish colour and by the end was a lighter colour. The start temperature for the three electric hot plates was at maximum (corresponding to #6 on their dials). The temperature was lowered to medium (#3) at about 11:47, when scum no longer appeared. Lids were then placed the pots with slight air space, and the contents gently boiled between11:50 until 13:30. At that time, the skin had begun to come off the bones, and the hot plates were turned to minimum heat (#1), it was noted that the water was reduced to approximately half the amount present initially. At 14:44 500ml was added to each of the two small pots and 1 liter to the biggest pot and the water was kept at a simmer for another 20mins. By this time it was possible to see that the largest pot had boiled too much and the contents were burned at the bottom. Altogether three hours was the time needed for fully cooking the calves' feet.

The two pots that had the good gelatine were poured into plastic bowl through a sieve and then into a stainless steel pot through a sieve again. The total weight of liquid was 1425.5 grams. The liquid from the large large pot was brown-yellow and weighted 843.2 grams and because it was burned, it was rejected. The liquid gelatine was allowed to cool to approximately room temperature (20ºC). At 18:05 both pots were covered and placed in domestic refrigerator at 4ºC and left overnight. On the following day the gelatine was weighted with the fat. The good gelatine weighted 2516.4 grams without lid (the burned gelatine weighted 2420.5 grams). A total of 125.8 grams of fat was removed from the good gelatine leaving a total weight of 2379.3 grams of useable gelatine.

The next step involved removing the sediment that was attached at the bottom of the jelly with a palette knife. At room temperature the gelatine was an almost solid gel. The recipe mentions using sugar and eggs, but these ingredients were not used since they would alter the properties of the jelly as well as they would be considered additives and influence the final result. By 12:02 the hot plate was dialed on #4 to slowly heat the gelatine until it was liquid. At 12:11 foam appeared, and it was decided to turn the heat down to #3. A teacupful of cold water (280 mls) was poured at 12:13 and the pot was brought very slowly to heat (#4 dial on plate) for 20 minutes. The liquor was left to cool for 45 minutes (the recipe said 30 minutes).

Meanwhile, boiling water was poured on a jelly cloth to warm it. The cloths left to boiled in the water (for 1 minute) and then cooled enough to handle and lastly wrung out.

The last step was to pour the gelatine through the jelly cloth into a stainless steel pot. The gelatine went right through the cloth and looked the same very milky (turbid) with a light colour. The gelatine was filtered again (while still warm) through 2 paper coffee filter bags supported in a glass funnel. Three glass funnels were used at once. Although this procedure was done two times not a lot of change was noticed except the gelatine twice filtered look markedly more yellow in colour but still turbid (like skimmed milk).

APPENDIX IX – SAMPLE CODES

Appendix IX.1 – General Sample Codes

Table IX.1 – Samples codes for reconstructions.

Source	Sample Code	Quantities Specified	Ingredients	Aim	Date Made
V= Vibert [5]	**V.PG**	-	**PG**= Pure Gelatine	-	06-Feb-15
	V.G1	Yes, except alum	**G1**= Gelatine, acetic acid (glacial), water, alcohol and alum	Render gelatine liquid	06-Feb-15
	V.G1v	Yes, except alum	**G1v**= Gelatine, acetic acid (vinegar), water, alcohol and alum	Render gelatine liquid	10-Feb-15
	V.G1a	No	**G1a**= Gelatine (V.G1) and glycerine	Render gelatine supple	06-Feb-15
	V.Ga	No	**Ga**= Gelatine and glycerine	Render gelatine supple	10-Feb-15
	V.GBs	No	**GBs**= Gelatine and bleached shellac	To add strength	10-Feb-15
	V.GRs	No	**GRs**= Gelatine and red shellac	To add strength	10-Feb-15
	V.GBx	No	**GBx**= Gelatine, bleached shellac and borax	To add strength	-
	V.GBP	Yes	**GBP**= Gelatine and bichromate of potash	Render gelatine insoluble, although the layer will be yellow	06-Feb-15
	V.GAl	No	**GAl**= Gelatine and Alum	-	06-Feb-15
	V.GAA	No	**GAA**= Gelatine and Aluminium Acetate	-	15-Apr-15
	V.GTRf	Yes	**GTRf**= Gelatine, turpentine and rice flour	Not specified	10-Feb-15
	V.G1.SCG	Yes, except alum	**SCG**= Gelatine, acetic acid (glacial), water, alcohol and alum	-	06-Feb-15
	V.G1.MCG	Yes, except alum	**MCG**= Gelatine, acetic acid (glacial), water, alcohol and alum	-	06-Feb-15
D= Davies [51]	**D.GS**	Yes	**GS**= Gelatine and bleached shellac	Render non-absorbent	15-Apr-15
-	**GRis**	-	**GRis**= Gelatine and rice starch (uncooked)	-	06-Feb-15
-	**GPos**	-	**GPos**= Gelatine and potato starch (uncooked)	-	11-Feb-15

Appendix IX.2 – Stepped Proportions of ingredients

Table IX.2 – Samples codes regarding number of layers applied to each square of canvas.

LOOM A				
Sample Code For layers applied	**Composition**	**Proportions**	**Observations of preparation**	**Observation during application**
V.PG-1	Gelatine and water.	Approximately 320g gelatine and 4460g water, which gives ~7% solution.	Light yellow gel, becomes jelly when cooled.	One layer applied. Spread well as a gel.
V.PG-2				Two layers applied. Spread well as a gel.
V.PG-3				Three layers applied. Spread well as a gel.
V.PG-4				Four layers applied. Spread well as a gel.
V.PG-5				Five layers applied. Spread well as a gel.
V.PG-6				Three times in sections, approximately 2-3cm at a time. Spread well as a gel.
V.G1-1	Gelatine, acetic acid (glacial), distilled water, ethanol (95%) and alum.	100g gelatine; 37.5g acetic acid (glacial); 37.5g distilled water; 25 g ethanol (95%) and 0.1g alum.	Light yellow liquid. It is rendered liquid as said in recipe. Does not get jelly when cooling.	One layer applied. Threads of canvas absorb liquid. Does not form film as PG.
V.G1-2				Two layers applied. Threads of canvas absorb liquid. Does not form film as PG.
V.G1-3				Three layers applied. Threads of canvas absorb liquid. Does not form film as PG.
V.G1-4				Four layers applied. Threads of canvas absorb liquid. Does not form film as PG.
				Five layers applied. Threads of canvas absorb

V.G1-5				liquid. Does not form film as PG.
V.G1v-1	Gelatine, acetic acid (biological culture), water, ethanol 95% and alum.	Same as V.G1 but with vinegar instead of acetic acid (glacial).	Light yellow liquid, similar to V.G1. Does not get jelly.	One layer applied. Covers majority of holes from canvas.
V.G1v-2				Two layers applied. Covers majority of holes from canvas.
V.G1v-3				Three layers applied. Covers majority of holes from canvas.
V.G1v-4				Four layers applied. Covers majority of holes from canvas.
V.G1a-1	V.G1 and glycerine	5gr V.G1; 1 drop (~0.03g) glycerine	Light yellow liquid as G1. Does not jelly when cooling.	Three times in sections at a time. Spread well and liquid. No significant changes noted in different drops of glycerine. There is no layer formation.
V.G1a-2		5g V.G1; 2 drops (~0.06g) glycerine		
V.G1a-3		5g V.G1; 3 drops (~0.09g) glycerine		
V.G1a-4		5g V.G1; 4 drops (~0.12g) glycerine		
V.Ga-1	Gelatine and glycerine	5g gelatine; 1 drop (~0.03g) glycerine	Very similar to PG and increased suppleness as more drops were added. Becomes jelly when cooling.	Identical viscosity of PG. Easy to spread with layer formation
V.Ga-2		5g gelatine; 2 drops (~0.06g) glycerine		
V.Ga-3		5g gelatine; 3 drops (~0.09g) glycerine		Spreads well, starts to get supple and there is a layer formation.
V.Ga-4		5g gelatine; 4 drops (~0.12g) glycerine		Easy to spread and supple, with layer formation.
V.GBs-1	Gelatine and bleached shellac (in ethanol)	1g gelatine; 3g bleached shellac	The liquid solutions turned from a light yellow to an orange colour.	Coarse solution, not very fluid and hard to spread.
V.GBs-2		1g gelatine; 4g bleached shellac		Less coarse than BS1 but difficult to spread evenly.
V.GBs-3		1g gelatine; 9g bleached shellac		Less coarse solution. Spreads more evenly than BS1 and BS2.

V.GRs-1	Gelatine and red shellac (in ethanol)	1g gelatine; 3g red shellac	The liquid solutions turned from a light yellow to a brown colour. Becomes jelly when cooling.	Enable to apply. The solution coagulates and gets hold to the brush
V.GRs-2		1g gelatine; 4g red shellac		Partial coagulation but applicable on canvas. Although does not make an uniform layer. Coarse liquid.
V.GRs-3		1g gelatine; 9g red shellac		Very viscous but fairly easy to apply. Fills most of the holes of canvas.

V.GAl-0	Gelatine and alum	5g gelatine; 0.1g alum	Solutions with a light yellow colour, identical to PG. Become jelly when cooling.	Harder to apply to get to fill holes than others GAl
V.GAl-1		5g gelatine; 0.0104g alum		Easy to apply. Flowing properties similar to V.PG
V.GAl-2		5g gelatine; 0.0052g alum		
V.GAl-3		5g gelatine; 0.0026g alum		
V.GAl-4		5g gelatine; 0.0013g alum		
V.GAl-5		5g gelatine; 0.0007g alum		Very fluid, easy to apply as V.PG.
V.GAl-6		5g gelatine; 1g alum	The solution is the whitest when compared to the others. Becomes jelly when cooling.	Coagulated partially due to temperature. After warming again solution was more viscous, like a gel. Did not saturated canvas, just a white layer on top. Does not stay fluid long, since it is terribly sensitive to temperature and starts to coagulate as soon as it cools.

V.GBx-1	Gelatine, bleached shellac with borax in water	6g bleached shellac; 1g borax and 50g distilled water	The solution containing the shellac, borax and water did not dissolve (gum aspect) after three attempts.	-

LOOM B				
Sample Code	**Composition**	**Proportions**	**Observations of preparation**	**Observation during application**
V.G1.SCG-1 **V.G1.SCG-2** **V.G1.SCG-3**	3 sheets of commercial gelatine, acetic acid (glacial), distilled water, ethanol 95% and alum	10g gelatine sheets in 100g distilled water; After 30 mins gelatine absorbed 52g of water. 19.5g acetic acid; 19.5g distilled water; 13g ethanol were added.	Very light yellow liquid, similar to V.G1. Does not get jelly.	Three layers applied. Threads of canvas absorb liquid. Does not form film as PG.
V.G1.MCG-1 **V.G1.MCG-2** **V.G1.MCG-3**	3 sheets of commercial gelatine, acetic acid (glacial), distilled water, ethanol 95% and alum	10g gelatine sheets in 100g distilled water; 7.5g acetic acid; 7.5g distilled water; 5g ethanol	Very light yellow liquid, similar to V.G1. Does not get jelly.	Three layers applied. Threads of canvas absorb liquid. Does not form film as PG.
V.GBP-0	Gelatine and bichromate of potash	20g gelatine; 4g bichromate of potash	The liquid is of a very orange tonality. Becomes jelly when cooling.	Easy applied on canvas, although some minor grains from bichromate of potash did not dissolve and got held between threads.
V.GBP-1		20g gelatine; 2g bichromate of potash	First dilution is liquid and very orange, becomes jelly when cooling.	Easy applied on canvas. Very liquid and threads absorb solution. Does not form a layer.
V.GBP-2		20g gelatine; 1g bichromate of potash	Second dilution needs to be warmed before use, since its solid. Light orange colour.	Easy applied on canvas. Very liquid and threads absorb solution. Does not form a layer.
V.GBP-3		20g gelatine; 0.5g bichromate of potash	Third dilution needs to be warmed before use, since its solid. Yellow colour.	Easy applied on canvas. Very liquid and threads absorb solution. Does not form a layer.
V.GBP-4		20g gelatine; 0.25g bichromate of potash	Fourth dilution needs to be warmed before use, since its	Easy applied on canvas. The colour seen is not the same as the liquid from plastic container. Look

			solid. Yellow colour.	alike V.PG
V.GBP-5		20g gelatine; 0.13g bichromate of potash	Fifth dilution needs to be warmed before use, since its solid. Light yellow colour.	
V.GBP-6		20g gelatine; 0.07g bichromate of potash	Sixth dilution is solid. Needs to be warmed before use. Very light yellow colour.	The most diluted solution made a very good uniform film. The colour seen is not the same as the liquid from plastic container. It is almost like V.PG.

V.GAl-3	Gelatine and alum	5g gelatine; 0.0026g alum	Solutions with a light yellow colour, identical to PG. Become jelly when cooling.	Easy to apply. Flowing properties similar to V.PG
V.GAl-5		5g gelatine; 0.0007g alum		

V.GAA-3	Gelatine and Aluminium Acetate	5g gelatine; 0.0026g aluminium acetate	Solutions with a light yellow colour, identical to PG. Become jelly when cooling.	Easy to apply. Flowing properties similar to V.PG
V.GAA-5		5g gelatine; 0.0007g aluminium acetate		

D.GS-1	Gelatine and bleached shellac (7% solution in alcohol)	1g gelatine; 9g bleached shellac	Very liquid solution with brownish colour.	The threads absorb instantly the liquid without layer formation.
D.GS-2		3g gelatine: 7g bleached shellac	Partially coagulation of shellac with gelatine. Orange colour appearance.	Creates an emulsion that turns problematic when applying in the canvas, since the shellac gets held in the brush. Does not form a layer.
D.GS-3		5g gelatine; 5g bleached shellac	With same amount of both materials there is a bigger emulsion of the shellac. Yellowish appearance.	Similar to D.GS-2, but more small particles of shellac get attached in the brush. Does not form a layer.
D.GS-4		7g gelatine; 3g bleached shellac	Minor emulsions in solution. Yellow appearance.	Besides the formation of small emulsions, there is layer formation although with small particles of shellac.
D.GS-5		9g gelatine; 1g bleached shellac	The proportion of both materials is well established. There are no emulsions visible. Solution is yellow, similar to V.PG-1.	Best properties for the application in the canvas. No emulsions visible within the threads. Homogeneous and solid.

D.GS-1.1	Gelatine and bleached shellac (14% solution in alcohol)	1g gelatine; 9g bleached shellac	Very liquid solution with brownish colour.	The threads absorb instantly the liquid without layer formation.
D.GS-1.2		3g gelatine: 7g bleached shellac	Partially coagulation of shellac with gelatine. Orange colour appearance.	Creates an emulsion that turns problematic when applying in the canvas, since the shellac gets held in the brush. Does not form a layer.
D.GS-1.3		5g gelatine; 5g bleached shellac	With same amount of both materials there is a bigger emulsion of the shellac. Yellowish appearance.	Similar to D.GS-1.2, but more small particles of shellac get attached in the brush. Does not form a layer.
D.GS-1.4		7g gelatine; 3g bleached shellac	Minor emulsions in solution. Yellow appearance.	Besides the formation of small emulsions, there is layer formation although with small particles of shellac.
D.GS-1.5		9g gelatine; 1g bleached shellac	Since the shellac is at higher percentage, there are small emulsions formations in the solution. Solution is yellow, similar to V.PG-1.	Presents good properties for application in canvas, although there are minor emulsions of shellac due to higher percentage of this material. Nevertheless the layer is solid.

V.PG-3	Gelatine and water	7g gelatine; 93g water	Light yellow liquid, becomes jelly when cooled.	Three layers applied. Spread well and liquid.

PILOT SUPPORT A				
Sample Code	**Composition**	**Proportions**	**Observations of preparation**	**Observation during application**
GRis-1	Gelatine and rice starch	12.26g gelatine; 2g rice starch	Very white liquid formed. Gets jelly when cooling. Starch accumulates in bottom.	Easy to spread and apply. Forms an uniform layer overall.
GPos-1	Gelatine and potato starch	12.26g gelatine; 2g potato starch		

PILOT SUPPORT B				
Sample Code	**Composition**	**Proportions**	**Observations of preparation**	**Observation during application**
V.GAl-0	Gelatine and alum	5g gelatine + 0.1g alum	Solution with a light yellow colour, identical to PG. Become jelly when cooling.	Very fluid and easy to apply with palette knife.
V.GTRf-1	Gelatine, turpentine and rice flour	6.25g gelatine; 6.25g turpentine; 12.5g rice flour	Light beige colour solution. A little viscous and grainy.	Easy to apply with palette knife. Not as easy to apply on Melinex® because of the granules.

Appendix IX.3 – Diagrams of reconstructions

Figure IX.1 – Diagrams showing where samples are located on loomed canvas (top) and on foam cards with fabric (bottom).

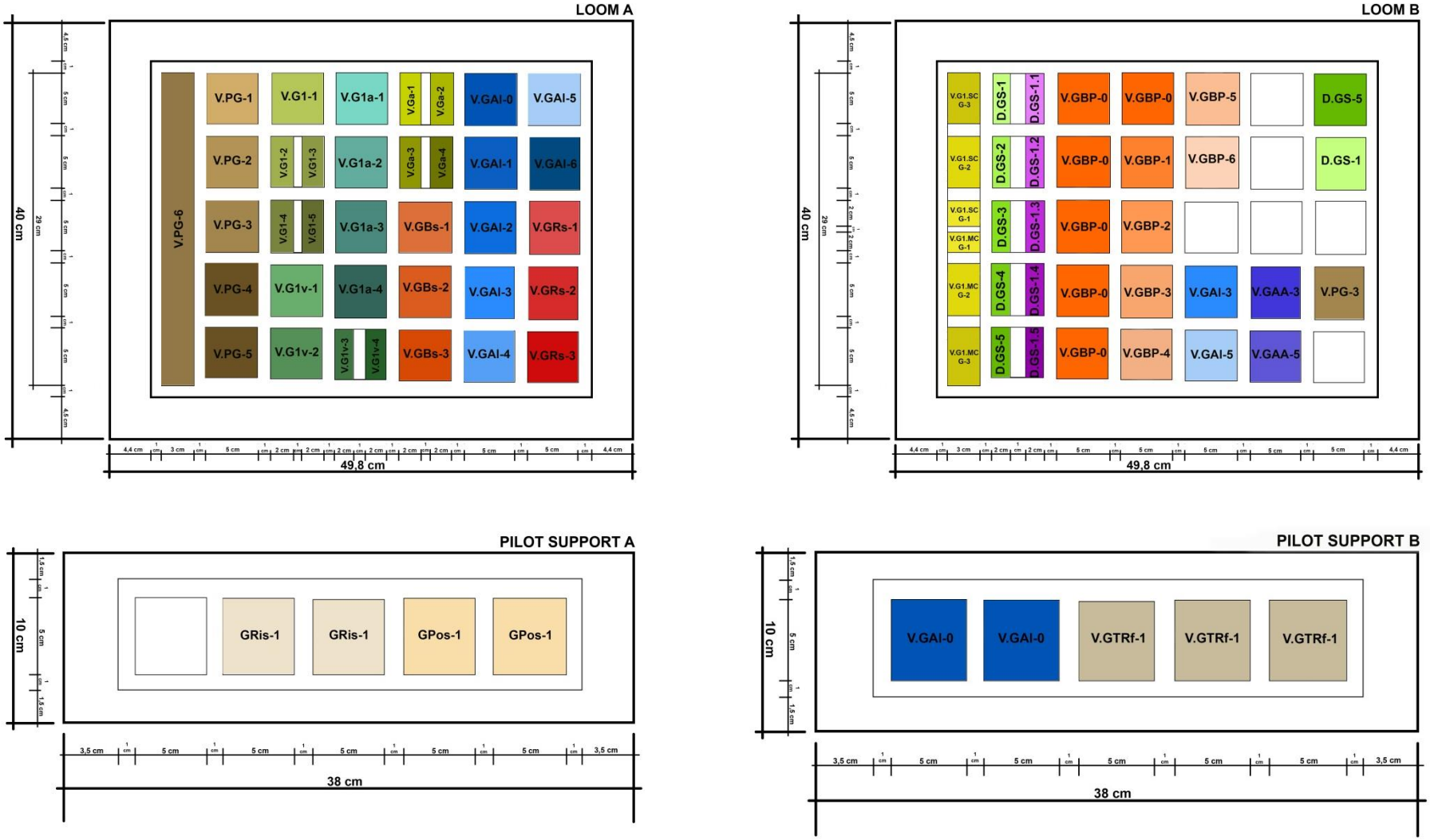
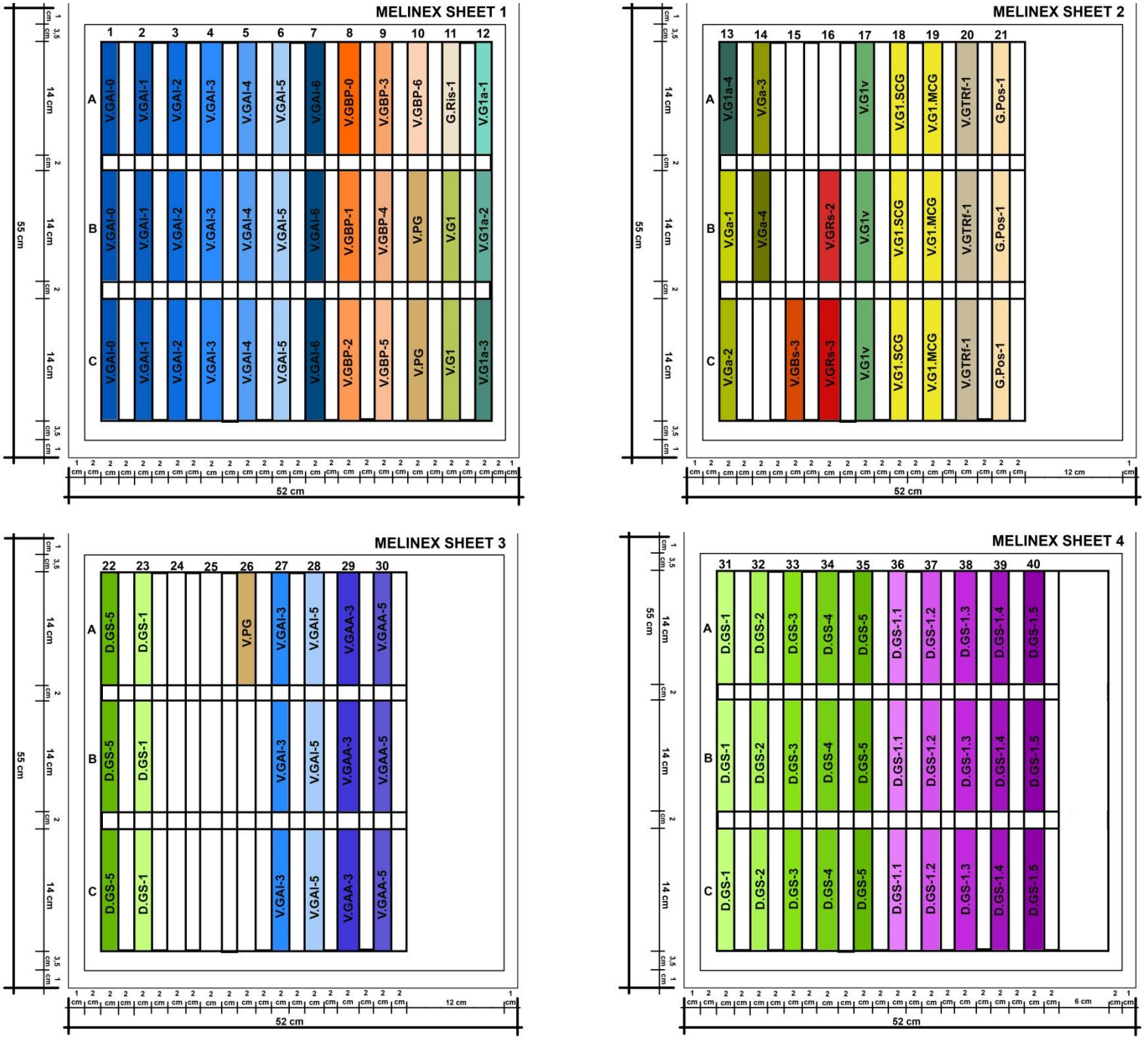


Figure IX.2 – Diagrams indicating where samples are located on all Melinex® sheets.



APPENDIX X – RECONSTRUCTIONS ANALYSIS

Appendix X.1 – Reconstructions Cross-sections. Normal and Ultraviolet light

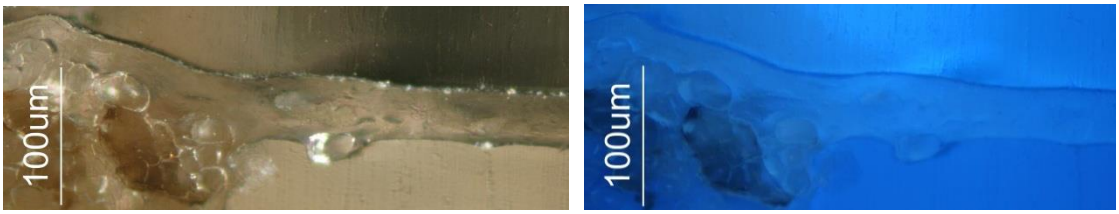


Figure X.1 - V.PG-3, pure calf's feet gelatine.

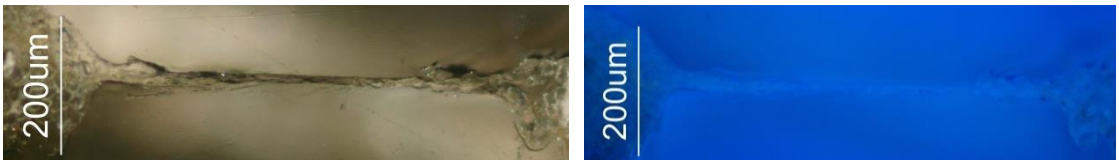


Figure X.2 - V.GAl-5, gelatine and alum.

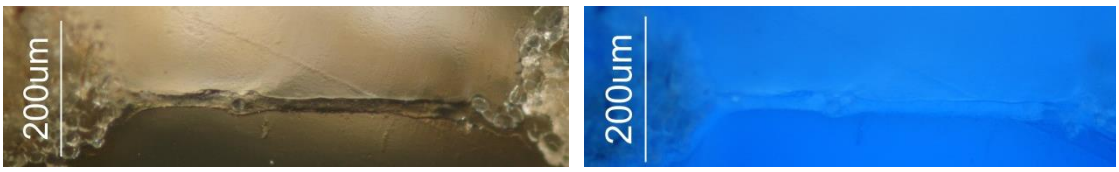


Figure X.3 - V.Ga-4, gelatine and glycerine.

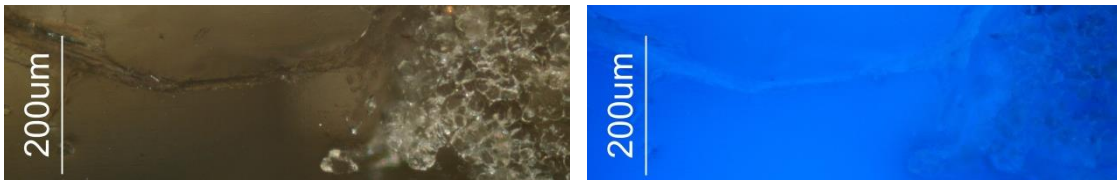


Figure X.4 - V.GBP-6, gelatine and bichromate of potash.

Figure X.5 - D.GS-5, gelatine and bleached shellac.

Appendix X.2 – Sensitivity tests

Table X.1 – Sensitivity test results.

Reconstruction- Sensitivity Tests						
Sample	**RH Test, 3 days at 99% RH**			**Water Test, cold water immersion**		
	Measurement before	Measurement after	Difference	Measurement before	Measurement after	Difference
ALUM V.GAI-0	**Overall:** 0.471mm x 0.429mm; **thickness:** 0.021mm	**Overall:** 0.382mm x 0.368mm; **thickness:** 0.039mm	**Overall:** 0.062mm^2; **thickness :** 0.018mm	Dissolved		
V.GAI-1	**Overall:** 0.418mm x 0.400mm; **thickness:** 0.032mm	**Overall:** 0.336mm x 0.329mm; **thickness:** 0.038mm	**Overall:** 0.057mm^2; **thickness :** 0.06mm	Dissolved		
V.GAI-2	**Overall:** 0.429mm x 0.386; **thickness:** 0.014mm	**Overall:** 0.355mm x 0.321mm; **thickness:** 0.025mm	**Overall:** 0.052mm^2; **thickness :** 0.011mm	Dissolved		
V.GAI-3	**Overall:** 0.375mm x 0.332mm; **thickness:** 0.014mm	**Overall:** 0.413mm x 0.374mm; **thickness:** 0.025mm	**Overall:** 0.03mm^2; **thickness :** 0.011mm	Dissolved		
V.GAI-4	**Overall:** 0.604mm x 0.452mm; **thickness:** 0.013mm	**Overall:** 0.510mm x 0.393mm; **thickness:** 0.021mm	**Overall:** 0.073mm^2; **thickness :** 0.008mm	Dissolved		
V.GAI-5	**Overall:** 0.371mm x 0.307mm; **thickness:** 0.014mm	**Overall:** 0.382mm x 0.360mm; **thickness:** 0.027mm	**Overall:** 0.024mm^2; **thickness :** 0.013mm	Dissolved		
V.GAI-6	**Overall:** 0.618mm x 0.468mm; **thickness:** 0.030mm	**Overall:** 0.404mm x 0.307mm; **thickness:** 0.041mm	**Overall:** 0.375mm^2; **thickness :** 0.011mm	Dissolved		
BICHROMATE OF POTASH V.GBP-4	**Overall:** 0.464mm x 0.414mm; **thickness:** 0.011mm	**Overall:** 0.446mm x 0.411mm; **thickness:** 0.016mm	**Overall:** 0.009mm^2; **thickness :** 0.005mm	**Overall:** 0.406mm x 0.369; **thickness:** 0.020mm	**Overall:** 0.447mm x 0.350mm; **thickness:** 0.022mm	**Overall:** 0.006mm^2; **thickness:** 0.002mm
V.GBP-5	**Overall:** 0.202 x 0.218mm; **thickness:** 0.012mm	**Overall:** 0.275mm x 0.232mm; **thickness:** 0.013mm	**Overall:** 0.019mm^2; **thickness :** 0.001mm	**Overall:** 0.504mm x 0.405mm; **thickness:** 0.016mm	**Overall:** 0.521mm x 0.463mm; **thickness:** 0.019mm	**Overall:** 0.037mm^2; **thickness:** 0.003mm
V.GBP-6	**Overall:** 0.432mm x 0.299mm; **thickness:** 0.011mm	**Overall:** 0.497mm x 0.309mm; **thickness:** 0.014mm	**Overall:** 0.024mm^2; **thickness :** 0.003mm	**Overall:** 0.444mm x 0.545mm; **thickness:** 0.011mm	**Overall:** 0.487mm x 0.534mm; **thickness:** 0.012mm	**Overall:** 0.019mm^2; **thickness:** 0.001mm
SHELLAC	**Overall:**	**Overall:**	**Overall:**			

D.GS-5	0.330mm x 0.354mm; **thickness:** 0.015mm	0.377mm x 0.330mm; **thickness:** 0.014mm	0.014mm^2; **thickness:** 0.001mm	The sample did not dissolve, although it was not possible to do the measurements after		
D.GS-1.5	**Overall:** 0.358mm x 0.414mm; **thickness:** 0.020mm	**Overall:** 0.362mm x 0.425mm; **thickness:** 0.022mm	**Overall:** 0.005mm^2; **thickness:** 0.002mm	**Overall:** 0.362mm x 0.290mm; **thickness:** 0.022mm	**Overall:** 0.358mm x 0.270mm; **thickness:** 0.014mm	**Overall:** 0.008mm^2 **thickness** 0.008mm
RICE STARCH GRis-1	Inconclusive since sample was very brittle	-	-	Dissolved		
POTATO STARCH GPos-1	Inconclusive since sample was very brittle	-	-	Dissolved		
V.GTRf-1	**Overall:** 0.401mm x 0.428mm; **thickness:** 0.036mm	**Overall:** 0.377mm x 0.448mm; **thickness:** 0.050mm	**Overall:** 0.03mm^2; **thickness:** 0.014mm	Dissolved		

Appendix X.3 – Reconstructions Analysis Table

Table X.1 – Analysis results from reconstructions.

Reconstructions Analysis					
Sample	**SEM-EDX**	**μ-FTIR**		**Py-GC/MS**	**Material Identified**
		Wavenumber (cm^{-1})	Assignment	Products found	
PURE GELATINE V.PG	-	3300(br); 3081m; 1650vs; 1546vs; 1454s; 1339m; 1241s	N-H stretching; C-H stretching; C=O stretching; C-N-H bending; C-H bending and 2x C-O stretching	Pyrolysis products of gelatine	Protein based material.
ALUM V.GAl-5	**C, O, Na, Cl, Al**, N, K, Ca, Si, S	3313(br); 3081m; 1650vs; 1550vs; 1454s; 1338m; 1241s	N-H stretching; C-H stretching; C=O stretching; C-N-H bending; C-H bending and 2x C-O stretching	-	By μ-FTIR it was not possible to detect the SO_4^{2-} anion from the alum structure, just a protein based material. However SEM-EDX indicated presence of Al.
V.GAl-6	-	3305(br); 3081m; 1652vs; 1540vs; 1454s; 1336m; 1240s; 1105s	N-H stretching; C-H stretching; C=O stretching; C-N-H bending; C-H bending; 2x C-O stretching and SO_4^{2-} stretching	-	By μ-FTIR it was possible to detect the SO_4^{2-} anion from the alum structure. Besides, the protein based material was also confirmed.
ALUMINIUM ACETATE	-	3300(br); 3080m; 1650vs; 1540vs; 1450s; 1400s; 1340m; 1250s	N-H stretching; C-H stretching; C=O stretching; C-N-H bending; C-H bending;	-	By μ-FTIR it was possible to detect the CO_3^{2-} ion from the aluminum acetate structure. Besides, the protein based material was also

V.GAA-5			CO_3^{2-} stretching; 2x C-O stretching		confirmed.
GLYCERINE V.Ga-1	-	3355(br); 3320vs;3081m; 2931m; 1650vs; 1546s; 1454s; 1403m; 1338m; 1241s; 1083w; 1041w; 925w; 856w	2x N-H stretching; 2x C-H stretching; C=O stretching; C-N-H bending; 2x C-H bending; 4x C-O stretching and 2x C-H bending	-	µ-FTIR confirmed the presence of both glycerine and protein based material.
V.Ga-4	-	3347(br); 3313vs; 3085m; 2927m; 1650vs; 1546s; 1454s;1403m; 1338m; 1241s; 1114w; 1045s; 921w; 856w	2x N-H stretching; 2x C-H stretching; C=O stretching; C-N-H bending; 2x C-H bending; 4x C-O stretching and 2x C-H bending	-	µ-FTIR confirmed the presence of both glycerine and protein based material.
BICHROMATE OF POTASH V.GBP-6	**C, O, N, Na, Cl**, Si, P, S, Cr	-		-	By performing SEM-EDX it was possible to confirm the presence of Cr.
SHELLAC D.GS-1	-	3422(br); 2390vs; 2857vs; 1735vs; 1715m;1 469m; 1251s; 1150w; 1110w; 1040w; 930w; 722w	N-H stretching; 2x C-H stretching; 2x C=O stretching; C-H bending; 4x C-O stretching; 2x C-H bending	Pyrolysis products of gelatine and shellac	µ-FTIR just confirmed the presence of a typical profile of shellac while Py-GC/MS identified the products of gelatine and shellac.
D.GS-2	-	-	-	Pyrolysis products of gelatine and shellac	By Py-GC/MS it was possible to confirm the presence of both gelatine and shellac products.
D.GS-3	-	-	-	Pyrolysis products of gelatine and shellac	By Py-GC/MS it was possible to confirm the presence of both gelatine and shellac products.
D.GS-4	-	-	-	Pyrolysis products of gelatine and shellac	By Py-GC/MS it was possible to confirm the presence of both gelatine and shellac products.
D.GS-5	-	3300(br); 3080m; **2930s**; **1720w**; 1653vs; 1547s; 1454s; 1340m; 1240s; **1080m**	N-H stretching; 2x C-H stretching; 2x C=O stretching; C-N-H bending; 2x C-H bending; 2x C-O stretching	Pyrolysis products of gelatine and shellac	µ-FTIR analysis indicated the same ''shoulder'' obtained in the portrait's size layer, with characteristic bands marked in bold. By Py-GC/MS it was possible to confirm the presence of both gelatine and shellac products.

APPENDIX XI – EQUIPMENT AND SUPPLIERS

Appendix XI.1 – Equipment

Product	Supplier	Date of Receipt
6 calves feet each cut in half (total of 12). Total weight: 7,75 kilos; 1,49 (€/kg).	Futuritalhos, Grupo Silau. Avenida Dr. Augusto Castro 12B, Lisboa. Contact: Carlos Povoas	Purchased 2-Feb-2015
Serra da Estrela, spring water. 2 bottles of 5 liters and 3 of 1,5 liters. Typical Analytical composition: Total mineralization (at 180ºC) mg/l:39 (±14); pH:5,8-7,0; Silica (SiO_2) mg/l: 17 (±5,5); Ions: Sodium (Na^+)mg/l: 4,4 (±1,1); Calcium (Ca^+)mg/l: 2,7 (±1,6); Bicarbonate (HCO_3^-)mg/l: 16,5 (±8); Chloride (Cl^-)mg/l: 3,2 (±0,9)	Sumol+Compal Marcas, S.A. Estrada da Portela 9, 2790-124 Carnaxide- Portugal. Costumer Service: 800 207 264	Purchased 2-Feb-2015
5 Stainless steel pots	West Band; Cuisinart; Italy Patent; Ikea	FCT-PNT Equipment
1. Electric hot plate: MOD. 240 EN with 2 plates, ø 145 mm and ø 180, 220V single-phase - 2500W, in enamelled steel with 6 position commutator and power indicator light. Weight 5.5 kg. 2.Electric hot plate: MOD. 180 EN with 1 ø 180 mm plate, 220V single-phase - 1500W, in enamelled steel with 6 position commutator and power indicator light. Weight 3.3 kg.	CTS Company http://www.ctseurope.com/en/index.php	FCT-PNT Equipment
Stainless steel sieve (2)		FCT-PNT Equipment
Metal basin		FCT-PNT Equipment
Glass Saucepan (2)		FCT-PNT Equipment
-Cheesecloth 274cm x 91cm, 100% cotton; -Kilner muslin square cloth 50cm x 50cm, 100% cotton	-Everyday Essentials, from Canada; -KILNER, established 1842, UK.	Purchased 2014 Purchased 2015
Home 7 Coffee filters nº4 (Pingo Doce) and Filter Lab 1240- circular plain with ø 12,5mm, 80gr/m^2	Pingo Doce market www.pingodoce.pt Filter Lab http://www.fanoia.com/inicio	FCT-PNT Stock
Filter funnels, plain acucurat 60º, short stern (3); one with ø 8 mm and two with ø 6mm.	Laborspirits, Rua Prof. Aires Sousa, 6A, 1600- 590 Lisboa. www.laborspirit.com	FCT-PNT Stock HTPA Stock
Beakers, tall form. 1000 ml (2); 250ml (2); 100ml (2); 50ml (5); 5ml (3)	Laborspirits, Rua Prof. Aires Sousa, 6A, 1600- 590 Lisboa. www.laborspirit.com	FCT-PNT Stock HTPA Stock
10x magnification optivisors	Donegan OptiVISOR http://www.doneganoptical.com/products/optivisor	FCT-PNT Stock

Heat Spatula:

Willards of Chichester, Sussex, England. Controller type 'E'. Serial No. 0471-479.

Appendix XI.2 – Suppliers

Product	Supplier	Date of Receipt
Gelatine extracted from calf foot	Futuritalhos, Grupo Silau. Avenida Dr. Augusto Castro 12B, Lisboa. Contact: Carlos Povoas	Purchased 2015
Commercial gelatin from blue box	Not specified.	FCT-PNT Stock
Glacial Acetic Acid	Sigma-Aldrich® www.sigmaaldrich.com	Photochemistry Laboratory (ORG 148) Stock
Distilled water, Type I Water Station, Diwer Technologies, 17cm Water; Water Max W1.	Faculdade de Ciências e Tecnologia, UNL, 2829-516, Caparica, Portugal	Inorganic Chemistry Stock
Ethanol 96% RPE 2,5L; UN 1170; 4146322	Carlo Erba Reagents S.A.S. BP616 F-27106 Val de Reuill Cedex	FCT-PNT Stock
Methanol, pure, 2L CH30 H, M=32.04g/mol	Pronalab®, Distribuidor: José M. Vaz Pereira, S.A, Rua da Madalena, 161-1100 Lisboa	FCT-PNT Stock
Sulfate Aluminium potassium dodecahydrate extra pure, Al K $(SO_4)_2.12H_2O$, 1kg, M=474,39 g/mol	E. Merck, D-6100 Darmstadt, F.R. Germany	HTPA (INORG 1) Stock
Aluminum acetate, basic hydrate, apprx $(CH_3CO_2)_2AlOH.{}_xH_2O$, 100g	Alfa Aesar® A Johnson Matthey Company. GmbH & Co KG. Zeppelinstrasse 7b. Tel:+49(0)721/84007-0	Purchased March 2015
Clearspring Organic White wine vinegar, aged in wood, 500ml	Clearspring.co.uk. Clearspring Ltd, London E3 7QE, UK.	Purchased January 2015
Glycerol (anhydrous)	Sigma-Aldrich® www.sigmaaldrich.com	Fotochemistry (ORG535) Stock
Gum lac- Red and Bleached	-	HTPA Stock
Shellac powder with borax # 60470	Kremer Pigmente GmbH & Co. KG www.kremer-pigmente.de	FCT-PNT Stock
Potassium dichromate, $K_2Cr_2O_7$, 1kg, Lote:148	Prepared by: Ceamed, Lda. Centro de Empresas e Inovação da Madeira- EV nº107, Madeira Tecnopólo,1º, 2020-105 Funchal, Portugal. Sold by LaborSpirit: Rua Prof Aires de Sousa 6-A, 1600-590 Lisboa. vendas@laborspirit.com	HTPA (INORG25) Stock
Rice flour wholemeal toast	Agricultura Biológica. Próvida, Produtos Naturais, Lda.	Purchased 2015
Turpentine 75ml	Daler-Rowney turpentine oil medium www.daler-rowney.com	Purchased 2015
Amidon de Riz en cristaux (Rice Starch), 250g	H.J. Heinz Belgium NV/SA B2300 Turnhout. www.artishistoria.com	FCT-PNT Stock
Potato Starch, Fécula de Batata, Produto Substancial, 200g	Productos alimentícios Zelly, José A. & C^{a}.Lda. Rua Fernando Tomás, 783-785, Porto, Portugal	Purchased February 2015
Rice Flour, Farinha de Arroz (integral torrada), 500g. Lote 20150831	Próvida® Produtos Naturais,Lda. Rua da Esperança, nº39, Raposeiras 2725-505 Mem Martins- Portugal. www.provida.pt	Purchased February 2015
Open weaved linen (2)	-	FCT-PNT Stock
1.Thick Melinex® sheet (100microns), polyester roll 1016mm x 20M roll, P415-100 2.Thin Melinex® sheet (25 microns), polyester roll 1016mm x 20M roll	PEL	FCT-PNT Stock
Scotch® Magic™ Tape 810	www.scotchbrand.com	FCT-PNT Stock
Stainless steel spatula	-	FCT-PNT Stock
Flat hogshair brush #8 (2cm long by 1,5cm wide)	-	FCT-PNT Stock
PB-72	-	FCT-PNT Stock
Beva371b	Gustav Berger's original formula 371b (Beva 371), Kremer Pigmente : http://kremer-pigmente.de/en	FCT-PNT Stock
Mowiol® 4-88	Kremer Pigmente: http://kremer-pigmente.de/en	FCT-PNT Stock
Kaolin, Kremer 58250	Kremer Pigmente: http://kremer-pigmente.de/en	FCT-PNT Stock
Chalk from Champagne, Natural Calcium Carbonate	Kremer Pigmente: http://kremer-pigmente.de/en	FCT-PNT Stock
Plasticine		FCT-PNT Stock